JOURNAL

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

VOLUME VI

1922-1923

1923

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

BOX 290, PENNSYLVANIA AVENUE STATION

WASHINGTON, D. C.

CONTENTS

PROCEEDINGS OF THE THIRTY-SEVENTH ANNUAL CONVENTION, OCTOBER, 1921

PAGE

SECOND DAY.

TUESDAY—MORNING SESSION.

REPORT ON CHEMICAL REAGENTS.

By G. C. Spencer (Bureau of Chemistry, Washington, D. C.), *Referee*.

Under date of May 25, 1921, the referee sent out 119 copies of a circular letter to members of the association who would be concerned with buying or testing the chemical reagents in their respective organizations. In this letter correspondence was requested relating to cases of unsatisfactory chemical reagents and the action which had been taken by the institution to secure a satisfactory adjustment of the trouble.

Only seventeen replies were received, and twelve of these had no suggestions or comments on the quality of reagents used. From the lack of response to this letter among the association members at large, it is assumed that the quality of reagents generally purchasable in this country is satisfactory. It is also assumed that in many of the chemical stations represented in this body the C. P. reagents are taken on faith and used without further testing; otherwise there would have been a keener interest manifested.

It is true that, taken altogether, the American manufacturers are putting out chemicals which can be accepted to a great extent on their face value and that they are keenly interested in bringing their products up to the highest possible standard of purity. To this end they have met in conference with each other and with members of the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society and have exchanged and considered suggestions relative to reagent standards.

No collaborative work was attempted as it was deemed advisable first to quicken an interest among the members in the quality of their reagents and especially to emphasize the desirability of reporting complaints regarding chemicals to the manufacturers. No such complaints were reported during the past year. If, however, they were made in the proper spirit, these complaints would be appreciated by the fair-minded dealers who would seek thereafter to give satisfaction, not only to the correspondent but to other purchasers.

Unfortunately, the analyses printed on the chemical labels are not always reliable, as the Bureau of Chemistry has learned during the eighteen years that it has been testing its purchased chemicals. This statement is not intended as a reflection on the honesty of the dealer, as

it is appreciated that it is impossible to state correctly the analysis of every bottle among the thousands that are daily shipped from the big factories; but in fairness to producer and consumer the fact should be plainly understood that the results on the labels are not dependable in every case.

The following criticisms of chemical reagents were received from association members during the past summer:

Acetone.—A sample was reported as containing about 40% of methyl alcohol.

Amyl Acetate.—This sample consisted largely of butyl and propyl acetates.

Calcium Carbonate, precipitated, of "tested purity".—The dealer's analysis showed the absence of potash, but potash was nevertheless found. The correspondent also complained that a heavy variety of calcium carbonate was difficult to obtain from dealers.

Iodine.—One sample was found to contain sulfur.

Powdered Iron.—This contained no impurities but was not properly screened.

Iron Reduced by Hydrogen and Sodium Carbonate.—Both were found to contain more impurities than the results printed on the labels seemed to warrant.

Sodium Carbonate.—Has also been found to run too high in chlorides.

Sodium Hydroxide.—Some samples were reported as containing so much carbonate as to make them objectionable for Kjeldahl work. Other samples of this chemical were much too high in chlorides and sulfates for satisfactory analytical work.

Sulfuric Acid.—In one case gave too high a blank for nitrogen determinations.

As the recent experience of the Bureau of Chemistry with certain reagents may be of interest your referee has copied the following items from the Information Sheet on Chemical Reagents, compiled in the Bureau in July, 1921:

Acetic Acid purchased by the Bureau has as a rule been very good. The limit of residue is 1 mg. per 100 cc. and the greater part of this residue is iron. Only occasionally is it possible to obtain an acid running as high as 99.9%, even though this percentage is claimed by the dealer. The acid strength is usually from 99.5 to 99.7%. The test for acid strength in this case is determined from the temperature of the congealing point.

Amyl Alcohol pure enough for use as a reagent in dyestuff or alkaloidal analyses has been difficult to obtain from American producers. One American firm, however, is at present offering a grade of the highest purity.

One of the branch laboratories of the Bureau has recently found soluble sulfates in the *Asbestos* that has been supplied for Gooch crucibles. Other samples of the asbestos have been found to contain no sulfates. This point is mentioned as a warning to the members of the association that asbestos should never be taken on faith but should be carefully tested before using.

U. S. P. Ether contains up to 3% ethyl alcohol and 1% of water. Particular attention is paid to the residue and more than 0.001% is never allowed in this or any other organic solvent.

The absolute *Ether* is as a rule very good. This will quickly develop peroxide if exposed to air and sunlight, but this peroxide formation may be entirely prevented by removing the ether from the can immediately and placing it over sodium.

The *Hydrochloric Acid* purchased in recent years has varied in acid strength from 33.5 to 36.5% and has contained more or less arsenic. Other impurities have generally

been absent. The residue, if any, has not exceeded 0.001%. Sulfuric acid is recommended for arsenic work as a substitute for hydrochloric as the good commercial grades are practically free of arsenic.

Zinc Sticks have always been somewhat unsatisfactory for arsenic determinations, and it is always advisable to run a sufficient number of blanks on all samples.

In conclusion, it is desired to emphasize a more extended use of the metric system of weights and measures. An effort has been made to have all chemicals put up in standardized packages of metric weight or volume. Chemical dealers have expressed a willingness to supply their products in metric units if the trade demanded it. All colleges, experiment stations and other parties who purchase chemicals have accordingly been requested by the American Chemical Society to state their future orders for chemicals in metric units and the General Supply Committee of the Federal Government has already adopted this policy so far as practicable. A representative list of unit packages of chemicals in common use has been prepared by W. D. Collins[1].

RECOMMENDATIONS.

It is recommended—

(1) That all members of this association make an effort to specify metric units when ordering new supplies of chemicals.

(2) That this association again declare itself in favor of urging all members to report unsatisfactory reagents to manufacturers during the coming year and to notify the secretary of this association of their action.

REPORT ON NON-ALCOHOLIC BEVERAGES.

By W. W. Skinner (Bureau of Chemistry, Washington, D. C.), *Referee*.

It was planned by the association last year that the referee should study a method for the analysis of those fruit products which are largely sophisticated. This is considered important work owing to the large trade in emulsified flavors and drinks prepared from them, in imitation of true fruit products, which has developed in the past two years. The Bureau of Chemistry found it necessary to issue a warning regarding the misbranding of such material.

It is necessary to differentiate between artificial flavors, imitations of true products, and the beverages made from true fruit extract.

Work has progressed, and a method has been formulated which it is thought will ultimately be of service. No collaborative work has been accomplished.

[1] *J. Ind. Eng. Chem.*, 1920, 12: 1206.

REPORT ON EGGS AND EGG PRODUCTS.

By H. L. LOURIE (Food and Drug Inspection Station, New York, N. Y.), *Referee.*

At the last meeting your referee reported that there seemed no possibility of determining whether or not dried egg products were decomposed unless a study of their composition was made at the point of production in order to obtain definite data as to the composition and character of the raw eggs used and the changes that take place during manufacture. It is well known, generally, that dried eggs are produced almost exclusively at the present time in China. The methods of production have been radically changed owing to the action of the Department of Agriculture in refusing admission to eggs which were contaminated with large amounts of zinc.

It is to be regretted that no methods which will conclusively show the use of decomposed material are available at the present time. The analyst must depend largely on the physical characteristics of the dried-egg product to determine whether or not it has been made from decomposed material. The methods for the determination of heavy metals are satisfactory as are those for the presence of preservatives.

As it was considered that it would be of great value, a tentative chapter on the methods of analysis generally used in government laboratories for the determination of the sanitary quality of liquid eggs has been prepared, including methods of analysis for liquid eggs, dried eggs and egg products. It was impossible for your referee to obtain collaborative action which would decide conclusively whether the methods proposed are acceptable or not. However, it should be pointed out that the Bureau of Chemistry has conducted a valuable piece of research work with respect to the examination of frozen egg products and interpretation of results under the direction of H. W. Redfield[1].

With respect to the analysis of egg products, the work of your referee has been confined to the analysis of materials such as egg noodles, in which the important consideration is to determine whether or not the quantity of eggs present is in compliance with the standards formulated by the Standards Committee for this commodity. There has been a great deal of discussion as to the accuracy of the Juckenack method for the determination of the amount of eggs and work done at the Bureau of Chemistry and at the New York and San Francisco Food and Drug Inspection Laboratories shows that this method does not give results which indicate the true amount of egg present. The difficulty that the investigator who attempts to devise new methods for the estimation of eggs in products of this type meets is that it is necessary to work out

[1] U. S. Dept. Agr. Bull. 846; 1920.

new ratios with respect to the lecithin P205 content of the various flours. There is a growing practice among manufacturers of egg noodles and similar products to use dried yolk or so-called dried whole egg mixtures which contain excessive amounts of yolk instead of whole egg which the standard set forth by the Department of Agriculture requires. The problem here is to prove that there is a deficiency in albumen derived from egg. It can readily be seen that a manufacturer using 5 per cent of dried yolk would obtain a product which, on analysis, would indicate from the lecithin P205 content that it contained much more than 5 per cent of whole eggs. Yet this product would be in violation of the standard which calls for 5 per cent of whole eggs.

The New York and San Francisco Stations and the Bureau of Chemistry have been working on methods to determine whether egg noodles are made from whole egg, yolky mixtures or yolk. This work has not been completed. With respect to the determination of lecithin P205, Jacobs and Rask have devised a method, based on the saponification of the fat, which recovers practically all of the lecithin P205 content in egg noodles. It has been noted that the lecithin P205 of flour and of egg solids, when determined by this method, is considerably higher than when determined by the Juckenack method; hence, different values for these constants must be inserted in the formula which is used for calculating the equivalent of egg solids from the lecithin P205 content of noodles. It should be noted that the values for this method, which are given in the following compilation of methods, are not based upon a sufficiently large number of determinations to be accepted as final.

FROZEN AND LIQUID EGG PRODUCTS.

TAKING OF SAMPLES.

Frozen egg samples shall consist, when possible, of original unopened packages. They shall consist of representative containers of the product in any individual shipment. Enough containers shall be taken to represent a whole shipment fairly. All samples shall be sent to laboratories in the quickest possible way. When transported by common carriers, samples shall be so packed as to prevent thawing and every precaution shall be taken to prevent delay in transit. They shall be delivered to the analyst immediately upon arrival at the laboratory and no sample shall be examined which does not arrive in a frozen condition. If the material is slightly melted around the circumference, the subsamples for bacteriological and chemical examination must be withdrawn from the portion which is still frozen.

When samples are opened, the bacteriologist, chemist, and microscopist shall all be present and, in case of official samples, shall initial and date seals and cans for identification in the regular manner.

In order to preclude all possibility of a claim of contamination during sampling, the bacteriologist shall always withdraw subsamples first when a container is opened. The chemist shall then withdraw subsamples. The remainder shall be turned over to the microscopist. Each analyst shall give a receipt to the one from whom the container was received, in the case of official samples.

For withdrawing subsamples, it will be found convenient to use a sterile butter sampler of sufficient length to enable one to remove a core of frozen material from the top to the bottom of the container, after first removing with a sterilized instrument (chisel) the surface layer of the frozen material.

If the sample is frozen very solidly, it may be found necessary to use a brace and long-shanked bit or ship-builder's auger and to collect the shavings for the sample.

Cores shall be taken midway between the center and circumference, from at least three widely separated parts of the container to form a composite sample.

Liquid egg samples shall be thoroughly mixed with a sterilized utensil such as a long-handled dipper which has been immersed (including the handle) in alcohol and flamed, and then subsamples withdrawn for examination. The subsamples for bacteriological examination must be placed in sterilized containers.

The chemical examination shall be started immediately after the taking of subsamples and all determinations shall be made in duplicate.

The subsamples are thawed by partially immersing the containers in warm water, the temperature of which should not be above 50°C. They must then be thoroughly mixed, preferably with an electric stirrer. In the absence of such an instrument in the chemical laboratory, the mixing may be quite satisfactorily accomplished by sucking the melted subsample several times through a Gooch crucible containing no asbestos, using very moderate suction. This mixed composite sample is examined by the methods which follow:

TOTAL SOLIDS.

Weigh approximately 5 grams of the sample into a tared lead dish of 2½ inches to 3 inches diameter and dry in a vacuum of not less than 25 inches at 55°C. until there is no further loss in weight. This drying usually requires about 4 hours. It is recommended that weighings be made at the end of 3½ hours' drying, and thereafter at intervals of about 30 minutes. Weigh to 3 decimal places. There is an appreciable gain in weight after the minimum has been reached. Express the results as per cent on the wet basis.

ETHER EXTRACT.

Extract the dry residue from the determination of solids with absolute ether, preferably in a Knorr apparatus, but if this is not available, in a Johnson extractor. Cut through the sides of the lead dish containing the solids at 4 equidistant points. Place the dish upon a fat-free filter paper. Flatten down the sides of the dish. Place another fat-free filter paper on top of the flattened dish and roll the papers and dish into a cylinder which will fit the extraction tube fairly snugly. In making the cylinder, turn in the ends in such a way as to prevent solid particles from dropping into the extraction flask. Place the cylinder in the extraction tube without any asbestos plug below it. If the extractor is working rapidly, 3 hours is sufficient to insure a proper extraction.

Distil off the ether from the extraction flask and dry the extract for one hour at 55°C. in a vacuum of not less than 25 inches. Weigh to 3 decimal places. Express the results as per cent on the wet basis.

The ether used should not contain any alcohol or water, as a higher result is obtained when either is present. It is, therefore, understood that ether freshly distilled from sodium will be used.

ACIDITY OF THE FAT.

Dissolve the fat obtained in the determination of ether extract in 50 cc. of neutral benzine to which has been added 2 drops of phenolphthalein indicator. Titrate with 0.05N sodium ethylate. Express the results as the number of cc. of 0.05N sodium ethylate required to neutralize 1 gram of fat.

AMMONIA NITROGEN.

Titration Method.

This method is an adaptation of Folin's method for the determination of ammonia in urine[1]. It consists essentially in making the sample alkaline, removing the liberated ammonia by aeration and catching it in a measured quantity of standardized acid. The excess acid is then titrated.

The apparatus consists of the following:

1. A wash bottle containing dilute sulfuric acid (about 35 per cent) to remove any ammonia that may be present in the air entering the system.
2. Some form of trap to prevent sulfuric acid being carried over mechanically.
3. An aerating cylinder about 50 mm. in diameter and 350 mm. high, fitted with a 2-hole rubber stopper carrying a right-angle air-inlet tube, open at the bottom and extending to within ½ inch of the bottom of the cylinder and a trap containing either a cotton or glass wool plug to prevent any liquid from being carried over mechanically.
4. An 8-ounce, wide-mouthed bottle fitted with a delivery tube coming from the trap on the aerating cylinder. It is not essential that the special ammonia absorption tubes be used. An ordinary glass tube with a small bulb blown on the end, through which a few holes are punctured, answers very well. The method of making these is given by Folin and Farmer[2].
5. A means of passing air through the system. This is best done by a pump which will furnish a blast with a pressure of 10 pounds per square inch and which discharges into a tank of sufficient size to compensate for the pulsations of the pump and to deliver a steady blast.

Suction may be used but it is not recommended.

Each of the first four parts enumerated is fitted with a 2-hole rubber stopper and all are connected by glass tubes of suitable shape and length to permit the proper passage of air through the apparatus. The tube leading into the acid wash bottle should contain a stop-cock for regulating the air supply.

Weigh approximately 25 grams of sample in a convenient container. Pour as much as possible of this material into the aeration cylinder and transfer the remainder by means of four 25 cc. portions of ammonia free water, stirring each time with a rubber-tipped glass rod to remove any egg adhering to the sides of the weighing vessel. Add 75 cc. of alcohol, mix well, let stand for 15 minutes. Add approximately 1 gram of sodium fluoride, 2 cc. of 50% potassium carbonate solution and 1 cc. of kerosene. Connect the apparatus and aerate into the receiving bottle which should contain 10 cc. of 0.02N sulfuric acid, 2 drops of methyl red indicator (saturated solution in 95% alcohol) and about 75 cc. of ammonia free water.

The aerations should be carried on for 4 hours or as long as necessary to remove all of the ammonia, using as rapid a current of air as possible.

Titrate the excess of acid with 0.02N sodium hydroxide (free from carbon dioxide). Express the results obtained as milligrams of ammonia nitrogen per 100 grams of sample on the wet basis.

If there is insufficient time to complete the determination, the sample may be left overnight in the cylinder with the alcohol and sodium fluoride added. The potassium carbonate should, of course, not be added until ready to proceed.

If the sample has a bad odor, it may be necessary to use more than 10 cc. of 0.02N sulfuric acid.

It is essential that a blank experiment be run to determine the percentage recovery of ammonia using a known amount of pure ammonium sulfate (containing about 3 mgs.

---

[1] *Z. physiol. Chem.*, 1902, **37**: 161.
[2] *J. Biol. Chem.*, 1912, **11**: 499.

of nitrogen) and 25 cc. of water, instead of the egg. For method of preparing pure ammonium sulfate see Folin and Farmer[1]. The recovery should be over 95 per cent.

It is also essential to run blank experiments with the reagents and water used.

REDUCING SUGARS.

Wash 25 grams of sample into a 200 cc. graduated flask with 75 cc. of water. Make slightly acid by adding 2 cc. of 5% acetic acid for white or whole egg and 1 cc. for yolk. Mix and immerse the flask in boiling water until the egg material is thoroughly coagulated. This requires about 15 minutes. Cool to room temperature and make up to the mark with washed alumina cream. Shake vigorously for 1 minute, allow to stand 5 minutes and then shake 1 minute. Filter through a dry folded filter and determine the reducing sugar in 50 cc. of the filtrate by the Munson and Walker method[2]. Calculate as dextrose and express the results as per cent on the wet basis.

The washed alumina cream is prepared by washing ordinary alumina cream 5 times by decantation, using enough water so that at least half of the total volume may be syphoned off each time.

On account of the volume occupied by the precipitate, the results are a trifle high. This error amounts to about 1.4 per cent for white, 3.3 per cent for whole egg and 7.0 per cent for yolk. It is not customary to correct for this.

INDOL AND SKATOL.

A 200 cc. portion of sample is diluted with 500 cc. of water, acidified with 40 cc. of 5% acetic acid for white or whole egg and 20 cc. for yolk, coagulated in boiling water or live steam and filtered. The filtrate is steam distilled as rapidly as possible. Extract the distillate (approximately 300 cc.) with ether in a separatory funnel. To the ether extract add about 3 cc. of water and evaporate before an electric fan until the smell of ether has almost but not entirely disappeared. A trace of ether does not affect the result. Add 10 cc. of water, filter and apply the following test to the filtrate:

Vanillin Test for Indol and Skatol.

To the solution to be tested add a few drops of a 5% solution of vanillin in 95% alcohol, and concentrated sulfuric acid. The acid should be added in the proportion of 2 cc. for each 5 cc. of solution being tested. If indol is present, an orange color will be formed which is soluble in chloroform, amyl acetate or amyl valerianate. If skatol is present, a deep red to violet color will be formed which is readily soluble in chloroform, amyl acetate or amyl valerianate[3].

As confirmatory tests, if needed, the following are suggested:

p-Dimethylaminobenzaldehyde Test.

To the solution to be tested, add 1 cc. of a solution consisting of 4 parts of paradimethylaminobenzaldehyde, 380 parts of absolute alcohol and 80 parts of concentrated hydrochloric acid, in such a way as to form two liquid layers. If indol is present, a purplish red color will be formed. If skatol is present, a blue violet color will be formed[4].

Herter's B-Naphtha Quinone Test.

Make test solution slightly alkaline with potassium hydroxide. Add 1 drop of a 2% solution of *B*-naphtha quinone sodium monosulfonate. If indol is present, a blue or green blue color will be formed[5].

---

[1] *J. Biol. Chem.*, 1912, **11**: 498.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 78.
[3] *J. Biol. Chem.*, 1916, **24**: 528.
[4] *Z. physiol. Chem.*, 1906, **47**: 25.
[5] *J. Biol. Chem.*, 1906, **1**: 257.

Pyruvic Aldehyde Test.

To the solution to be tested add a small crystal of ferric sulfate and a few crystals of pyruvic aldehyde. Then carefully run sulfuric acid down the inside of the container in such a way as to form a layer at the bottom. If indol is present, a red violet ring will form[1].

Dimethylaniline Test.

To the test solution add a few drops of dimethylaniline and sulfuric acid. If skatol is present, a deep red violet coloration is formed[1].

Glycolic Acid Test.

To the solution to be tested add a few crystals of glycolic acid and an equal volume of sulfuric acid. If skatol is present, a red violet color is formed[2].

PRESERVATIVES[3].

DRIED EGGS.

PHYSICAL CHARACTERISTICS.

Perform organoleptic tests. Note particularly the taste and odor of the product as it is. Place about 10 grams in a 100 cc. beaker, add 50 cc. of water, stir, cover with watch glass and let stand one-half hour. Note odor.

ZINC.

Place 25 grams of a well-mixed sample in an 800 cc. Kjeldahl flask; add 5 grams of zinc-free potassium sulfate, 3 to 4 glass beads to prevent bumping, 30 cc. of concentrated sulfuric acid, in the case of yolks or whole eggs (25 cc. of the acid in the case of albumens) and 30 cc. of concentrated nitric acid. Do not heat. When spontaneous action subsides, add 10 cc. of concentrated nitric acid. After 2 or 3 additions of concentrated nitric acid the action becomes less violent. Heat gently, at first, continuing the addition of concentrated nitric acid and increasing the temperature as the digestion proceeds until the contents of the flask are straw colored or colorless, after the nitric acid fumes have been boiled off. This digestion may be accomplished in the case of albumen in 40 minutes and in the case of yolks or whole eggs in 1 hour. To warm digestion add 100 cc. of water; pour into a 400 cc. beaker and rinse flask with two successive 50 cc. portions of water. To the combined water solution add concentrated ammonia to faintly alkaline. Pass hydrogen sulfide gas through solution for 15 minutes which should be sufficient to saturate. (At this point the majority of albumens indicate the presence or absence of zinc. In the case of albumen, if zinc is present, add 1 cc. of a diluted solution of ferric chloride containing 0.5 gram of solid ferric chloride per 100 cc. This will assist in retaining zinc sulfide on the paper when filtering. Pass hydrogen sulfide gas through the solution for 15 minutes.) Heat beaker on steam bath for one-half hour. Remove. Allow to settle from 5 to 10 minutes. Decant through 9 cm. filter paper allowing as much of the precipitate as possible to drain thoroughly. Dissolve the zinc sulfide from this precipitate with 10% hydrochloric acid, the solution after passing through the filter paper being returned to the original beaker. Copper and lead sulfide are insoluble at this point, and may be determined by the A. O. A. C. methods[4]. To the hydrochloric acid solution add 5 grams of ammonium chloride and excess of bromine water and a slight excess of concentrated ammonia.

---

[1] *J. Biol. Chem.*, 1916, **24**: 527.
[2] *Biochem. Z.*, 1919, **19**: 523.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 117.
[4] *Ibid.*, 151, 285.

Neutralize carefully with 10% hydrochloric acid adding 2 cc. in excess; add 10 cc. of 50% by weight of ammonium acetate and 8 to 10 drops of 10% ferric chloride solution, or enough to give a good reddish tinge. Dilute to about 300 cc. with water and boil for 1 minute. Settle; filter hot and wash with hot 5% ammonium acetate. Pass hydrogen sulfide gas through filtrate for 15 minutes. Heat one-half hour on steam bath; filter through weighed heavily padded Gooch crucible using gentle suction. Wash with hot 5% ammonium acetate solution. Dry in oven; then ignite, roasting first. Increased weight of Gooch is due to oxide of zinc. This multiplied by 0.8034 gives zinc present in 25-gram sample.

PRESERVATIVES[1].

EGG PRODUCTS.

EGG NOODLES.

MOISTURE.

Dry a convenient quantity of the sample, 2 to 3 grams, at the temperature of boiling water, in a current of dry hydrogen or in vacuo, until it ceases to lose weight (approximately 5 hours). The loss in weight is the moisture content.

ASH.

Char a convenient quantity of the sample, 5 to 10 grams, in a previously ignited and weighed platinum or silica dish and burn at the lowest possible heat until free from carbon. If a carbon-free ash can not be obtained in this manner, exhaust the charred mass with water, collect the insoluble residue on an ashless filter, burn until the ash is white or nearly so, and then add the filtrate to the ash and evaporate to dryness. Heat the residue to redness, cautiously at first to avoid decrepitation or spattering, cool in a desiccator and weigh.

SODIUM CHLORIDE IN ASH.

Determine chlorides by the silver nitrate gravimetric or the Volhard volumetric method. These methods are described in detail in any of the standard texts on quantitative analyses. Calculate to the equivalent of sodium chloride. Total ash, minus sodium chloride, is the salt-free ash.

NITROGEN[2].

FAT.

Treat 5 grams of the sample in a loosely stoppered 200 cc. Erlenmeyer flask with a mixture of 10 cc. of alcohol (95%), 2 cc. of concentrated ammonium hydroxide, and 3 cc. of water, keeping the contents of the flask at the boiling point for 2 minutes, preferably on the steam bath. After cooling, extract the contents of the flask with 3 successive 25 cc. portions of ethyl ether, mixing and tamping the material thoroughly each time with a glass rod flattened at the end and pouring the extracts off by decantation into a 250 cc. beaker. The last 25 cc. portion of ether should be drained out as completely as possible, after which another 15 cc. portion of the same ammoniacal alcohol solution is added to the flask and the matted material disintegrated as thoroughly as possible by means of the flattened glass rod which may be left in the flask for this purpose. The flask is then returned to the steam bath and the entire procedure repeated, the second set of ether extracts being poured into the beaker containing the first set. The second treatment with the ammoniacal alcohol mixture should be more gradual and somewhat longer than the first, so that the ether remaining in the flask

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 117.
[2] *Ibid.*, 7.

may be evaporated off and the ammoniacal alcohol brought to the required boiling point without results disastrous to the determination.

Evaporate the combined extracts to dryness on the steam bath and extract the fat from the residue left in the beaker with successive portions (5 or 6 treatments, using about 15 cc. each time) of a mixture of equal volumes of ethyl ether and petroleum ether. Collect the extracts in a tared platinum dish (do not try to filter), and evaporate to dryness on the steam bath. Dry the residue in a water-jacketed oven at the temperature of boiling water for 30 to 45 minutes, cool in a desiccator and weigh.

LECITHIN P2O5. METHOD I.

Add 3 cc. of a concentrated alcoholic solution of potassium hydroxide to the fat in the dish, as obtained in the preceding method. Evaporate to dryness, char, and determine total P205 by the volumetric method[1]. Owing to the small quantity of P205 in the fat from a 5 gram sample of noodles, it may be advisable in some cases to use the nephelometric method[2].

The following formula is used for calculating the percentage of egg solids in noodles on the moisture-free basis:

$$\frac{(A-0.0548)\times 100}{(1.38=0.0548)}=X,$$

in which A = percentage of lecithin P205 in the sample,
0.0548 = percentage of lecithin P205 in flour (dry basis),
and 1.38 = percentage of lecithin P205 in whole egg solids.

GASOLINE COLOR VALUE.

Place 20 grams of the sample in a wide-mouthed, glass-stoppered bottle of about 120 cc. (4 oz.) capacity, and add 100 cc. of colorless gasoline. Stopper tightly and shake vigorously for 5 minutes. Let stand for 16 hours, shake again for a few seconds until the flour has been loosened from the bottom of the bottle and thoroughly mixed with the gasoline, and then filter immediately through a dry 11 cm. paper into an Erlenmeyer flask, keeping the funnel covered with a watch glass to prevent evaporation. In order to secure a clear filtrate a certain quantity of the flour should be allowed to pass over onto the paper and the first portion of the filtrate passed through the filter a second time. It will be found convenient to fit the filter paper to the funnel by means of water, after which it should be dried thoroughly, either by letting stand overnight in a well-ventilated place or by heating.

Determine the color value of the clear gasoline solution in a Schreiner or Campbell-Hurley colorimeter, using for comparison a solution of potassium chromate containing 0.05 gram of potassium chromate per liter, conveniently prepared by making 10 cc. of an aqueous solution containing 0.5 gram of potassium chromate per 100 cc. up to 1 liter. The colorimeter tube containing the gasoline solution should be adjusted to read 50 mm., then the tube containing the standard chromate solution raised or lowered until the shades of yellow in both tubes match. The reading of the chromate solution divided by the reading of the gasoline solution gives the gasoline color value, the color of the standard chromate solution being considered as unity.

NOTES.

Standing for a longer time than that prescribed does not appear to affect the results. In fact, the filtration may be dispensed with entirely if the solution is allowed to settle after the second shaking until perfectly clear, which usually requires at least 24 hours.

The color value may be determined also in Nessler tubes, using for comparison

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 3.
[2] *J. Biol. Chem.*, 1918, **36**: 335.

potassium chromate solutions of various dilutions prepared from the stock solution (containing 0.5 gram per 100 cc.), and filling the tubes in all cases to the height of 50 mm., or (less accurately) in a Lovibond tintometer. In the latter case the color value is obtained directly, the solution of potassium chromate containing 0.05 gram per liter corresponding in color to the 1.0 of the yellow slide. In order to avoid confusion the color value should be referred to the potassium chromate solution containing 0.05 gram per liter in all cases.

If an approximate result is sufficient for the purpose, it may be obtained by carefully pipeting off the clear, supernatant gasoline solution before the second shaking. The results thus obtained are about 10% lower than those obtained by the standard method as just given.

ARTIFICIAL COLOR.

Hertwig's Method[1].

Macerate with a pestle in a 6-inch mortar 75 grams of the finely ground sample with 40 cc. of hydrochloric acid (1 to 1). A fairly stiff mass results but no more acid should be added. Continue the maceration until all particles are moistened and the entire mass is homogeneous. Then add 60 to 70 cc. of amyl alcohol and again macerate well, in the cold, until most of the color is apparently extracted. The time necessary for this depends upon the kind of color and its amount, but 5 to 10 minutes is usually sufficient. Filter the mixture on a folded filter paper or on a Büchner funnel using suction. Much of the excess of alcohol may be forced out by pressing down on the material on the filter with the pestle. The filter paper and residue may then be enclosed in a cloth and the greater part of the remaining alcohol pressed out. In order to remove all color the exhausted sample may be returned to the mortar and re-extracted with 30 to 40 cc. of fresh amyl alcohol and filtered as before. Two such extractions will remove most of the color and three will leave the material being extracted almost perfectly white. The amyl alcohol will contain the color in a fairly pure condition.

Wash the amyl alcohol with 20 cc. of hydrochloric acid (1 to 1), then remove the color fractionally by successive washings with hydrochloric acid of decreasing strengths such as 4 N, N, 0.25 N, etc. Warming the acid is recommended. The color or colors so removed may be identified by Mathewson's method[2]. Attention is particularly called to the directions on pages 18 to 20 of this bulletin under the caption of "Abridged Procedure for Permitted Dyes Only".

Many colors will be colorless in acid amyl alcohol and not apparent to the eye until washed out and the solution neutralized.

NOTES.

This method seems capable of extracting small quantities of color very thoroughly from pastes. The procedure is very simple and the extraction takes little time. The extracted color is fairly free from foreign interfering substances and in a condition suitable for specific tests for its identification.

Jablonski Method[3].

Macerate 250 grams of the sample (depending upon the quantity of color present), with alcohol of a strength of about 80% by volume and made slightly alkaline with ammonia. Continue the maceration until the color is extracted, if necessary warming on the steam bath. Filter and evaporate the filtrate until the alcohol is expelled and then add about one-fourth its volume of 25% salt solution, cool if necessary, and extract with gasoline or ether. The solvent will extract saffron, annatto, turmeric and all

[1] Devised by Raymond Hertwig.
[2] U. S. Dept. Agr. Bull. 448: (1917).
[3] Devised by C. F. Jablonski.

oil-soluble colors, also fats. Draw off the aqueous layer and wash the solvent with 5% salt solution adding the washings to the water solution. If the aqueous layer and washings are colorless no other colors are present.

Saffron, annatto and turmeric may be removed from the gasoline (or ether) with 70% alcohol and the usual tests applied. Any oil-soluble colors, if suspected, may be fractionally separated and identified by Mathewson's method.

If colored, extract the remaining aqueous solution and washings with amyl alcohol. This will remove the common orange colors, Orange I, Orange II, and Crocein Orange (S. & J. Nos. 85, 86 and 13, respectively), also Martius Yellow (S. & J. No. 3). Separate the aqueous layer and wash the amyl alcohol 2 or 3 times with a 5% salt solution to remove small amounts of Naphthol Yellow S and add the washings to the aqueous solution. If the aqueous solution is colored Naphthol Yellow S or Tartrazine may be suspected. Naphthol Yellow S may be removed by extraction with amyl alcohol after acidifying to approximately 1/64N with hydrochloric acid. If, after this treatment, any color remains in the aqueous solution strongly acidify it with hydrochloric acid and again extract with amyl alcohol. Tartrazine will be extracted.

The advantage of the procedure as outlined above is the easy separation of the various color groups as well as a partial elimination of the protein material which usually causes trouble with other alcoholic extraction methods.

Modification of the Jablonski Method[1].

Macerate 250 to 500 grams of the sample, depending upon the quantity of color present, with alcohol of a strength of about 80% by volume made slightly alkaline with ammonia. Warm on the steam bath in order to insure sufficient extraction of color. Filter with suction upon a Büchner funnel and evaporate the filtrate until most of the alcohol has been expelled and the consistency is that of cool molasses. Take from the steam bath and add about an equal volume of low boiling petrolic ether. Also add a large pinch of coarse sand. Stir the mixture until homogeneous and again place upon the steam bath, taking care that the petrolic ether does not evaporate too quickly. From time to time when it is noticed that practically all of the petrolic ether has evaporated add additional quantities, performing this operation until such time as the mass assumes a spongy, jelly-like consistency and the odor of alcohol is faint. Take from the steam bath, spread the product as well as possible upon a large watch glass and place in the hot water oven. Continue the heating until such time as the product is dry and tough. It may then be scraped from the glass and ground in a mortar. Pour the ground mass into a separatory funnel and add about half of its volume of 25% salt solution. At this point it is advisable to pour into the separatory a few cc. of small lead shot. This helps to disintegrate the mass upon extraction with gasoline. The method may then proceed in the same manner as stated in the Jablonski method.

The advantage of this modification depends upon the fact that emulsions due to gluten are avoided. No special care need be observed in the amount of added ammonia and, provided the alcohol is finally removed, separations proceed easily.

RECOMMENDATIONS.

It is recommended—

(1) That the following methods given under the examination of frozen and liquid egg products be adopted as tentative methods:

Total Solids	Titration Method for Ammonia Nitrogen
Ether Extract	Reducing Sugars
Acidity of Fat	Indol and Skatol.

[1] By M. G. Wolf.

(2) That the following methods of analysis under "Egg Products", sub-heading "Egg Noodles", be adopted as tentative methods:

Fat Lecithin P205, method by Jacobs and Rask.

(3) That during the coming year, the referee conduct collaborative work with respect to the determination of heavy metals, especially zinc, in dried eggs, and that collaborative work be conducted with respect to the determination of fat and lecithin P205 in egg noodles using the methods of Jacobs and Rask.

(4) That no further work be done on the Juckenack method for lecithin P205 since investigative work at three widely separated laboratories of the Bureau of Chemistry has shown this method to give low results.

NOTE.—Your referee can not see the value of conducting collaborative work with respect to the methods of analysis employed in the examination of frozen and liquid eggs since the research work conducted and already published by the Bureau of Chemistry[1] amply covers the field and represents a type of collaborative work that would be practically impossible for any referee to conduct for the association.

REPORT ON PRESERVATIVES (SACCHARIN).

By MILTON G. WOLF (U. S. Food and Drug Inspection Station, New York, N. Y.), *Referee.*

Your referee regrets that he was unable to conduct any collaborative work on methods for the determination of saccharin in foods. However, the details of a new method for the determination of saccharin in bread, cake and similar products have been worked out. This method deals largely with improvements with respect to the preparation of the sample before the final extraction with ether.

An improved method for the detection of small amounts of coal-tar dye in alimentary products led to the belief that the same ideas might be used to advantage in the quantitative estimation of saccharin in baked-food products. The directions are as follows:

A water-alcohol mixture appears to be the only efficacious solvent of the saccharin which has been incorporated in the bread; the water moistens the bread while the alcohol dissolves the saccharin. When this mixture, containing the saccharin filtered from the bread, is evaporated, the gluten, which at first was soluble, forms into a characteristic gelatinous mass from which ether, the final solvent, does not extract the saccharin quantitatively. To obviate this, heat the hydroalcoholic solution on the steam bath in a beaker until most of the alcohol is evaporated and the product has the consistency of molasses. Take from the steam bath and add about an equal volume of low boiling petrolic ether and a few pinches of coarse sand. Stir the mixture until homogeneous and again place upon the steam bath, taking care that the petrolic ether

[1] U. S. Dept. Agr. Bull. 846: (1920).

does not evaporate too rapidly. When it is noticed that practically all of the petrolic ether has evaporated, add an additional quantity, repeating this operation until the mass assumes a spongy, jellylike consistency, and the odor of alcohol is faint. Take from the steam bath, spread the product upon a large watch glass and place in the hot water oven. Heat until the product is dry and tough. It may then be scraped from the glass and ground in a mortar. Extract the resultant product, to which has been added a few grams of lead shot, with ether by the usual method and determine saccharin quantitatively by the usual fusion method[1].

Although it has not been possible to conduct sufficient determinations to state positively that this method will obtain all the saccharin present, it is believed, in view of the difficulty Seeker and the referee[2] met in their research on saccharin, with respect to its determination in various types of so-called diabetic breads to which known amounts of saccharin had been added, that this method will obviate some of the difficulties encountered and may yield satisfactory results.

RECOMMENDATIONS.

It is recommended—

(1) That for the coming year the referee prepare a list of the methods commonly used in the estimation of saccharin.

(2) That the referee conduct collaborative work on those methods which previous work done by the association has shown to give good results.

REPORT ON FOOD COLORS.

By W. E. Mathewson[3] (Bureau of Chemistry, Washington, D. C.), *Referee.*

The association's investigational work on food colors comprises two somewhat different lines of study which relate, respectively, to the examination of colored food products and commercial food coloring preparations.

Chapter X of the official methods[4] deals chiefly with the qualitative examination of foods colored with coal-tar dyes and gives a comparatively full discussion of this phase of the subject. Further study of the coloring matters of the common fruits and vegetables must be made before a coherent scheme of analysis can be devised that will provide for the complete identification of all coloring matters in food products. The researches of Willstätter and his co-workers are rapidly extending our knowledge of the so-called natural colors. Willstätter and Schudel[5] have discussed the qualitative analyses of mixtures containing such

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 122.
[2] *J. Assoc. Official Agr. Chemists*, 1917, 3: 38.
[3] Present address, Bureau of Standards, Washington, D. C.
[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 131.
[5] *Ber.*, 1918, 51: 782. Schudel, Dissertation, Eid Tech. Hochscule, Zurich, 1918.

coloring matters, and it is to be hoped that some of the substances used by them as reagents and which are rather difficult to prepare in the laboratory will soon be placed on the American market.

The methods for the analysis of commercial coal-tar food dyes which were adopted tentatively last year were in the main edited from publications that had been in print for several years, and no doubt had come to the attention of most analysts engaged in this work. Sets of mimeographed sheets describing these methods were sent out last December to all chemists known to be engaged in the analysis of coal-tar food colors with the suggestion that they report any objectionable or incomplete statements either at this meeting or to the referee directly. No comments by letter were received other than those of R. E. Doolittle as chairman of Committee C. It is believed that further work on the analysis of these products may be directed profitably to the development of additional methods for the estimation of the commoner impurities in commercial dyes. The method for the estimation of small amounts of aromatic amino compounds, described in connection with this report, is of this class.

THE USE OF SODIUM-ALPHA-NAPHTHOL-2-SULFONATE FOR THE SPECTROPHOTOMETRIC ESTIMATION OF AROMATIC AMINO COMPOUNDS.

By W. E. Mathewson[1] (Bureau of Chemistry, Washington, D. C.).

The work described in this paper was undertaken in connection with the analysis of dye products contaminated with small amounts of aromatic amino compounds, and it is believed that the data obtained provide a basis for a fairly satisfactory analytical method for the estimation of these and other substances that can be smoothly converted into amino or diazo compounds by known reactions.

Reverdin and de la Harpe[2] and Hirsch[3] have described methods for the estimation of amines which depend on converting them into the corresponding diazo compounds and titrating the latter against standard solutions of naphthol derivatives, the first-named investigators using R-salt (sodium salt of 2:3:6 naphtholdisulfonic acid) the last, Schaeffer's salt (sodium salt of 2:6 naphtholsulfonic acid). These processes, like most other well-known methods, are scarcely applicable when the amount of amine available is below one centigram. A direct adaptation of the same reactions for a quantitative colorimetric process is open to some objection or question because both R-salt and Schaeffer's salt,

---

[1] Present address, Bureau of Standards, Washington, D. C.
[2] *Chem. Ztg.*, 1889, 13: 387, 407; *Ber.*, 1889, 22: 1004.
[3] *Ber.*, 1891, 24: 324.

like other naphthol derivatives that couple in the ortho position, are not particularly reactive toward diazo compounds and hence may combine so slowly in dilute solutions that an appreciable proportion of the unstable diazo compound undergoes other changes; furthermore, with small amounts of amines the relative excess of nitrous acid present is much greater, and the possible action of this on the naphthol derivative with the formation of colored compounds must be considered. An examination of the larger handbooks on organic analysis indicates that reactions of this class have not come into favor for application to colorimetric methods.

However, the reactions leading to the formation of azo compounds have, undoubtedly, been studied more thoroughly than those involved in most other color tests or colorimetric methods for amines. Investigations of special interest are those of Hantzsch and Schümann[1] on the influence of concentration and temperature on the rate of diazotization of various amines; of Cain and Nicoll[2] on the rate of decomposition of diazo compounds; of Orton, Coates and Burdett[3] on the effect of light on diazo compounds; and of Goldschmidt and Merz[4] and Goldschmidt and Keppeler[5] on the coupling of diazo compounds with phenols and naphthols. The tinctorial power of the azo dyes is well known to be very high and of the same order as that of dyes of most other classes.

It was found in preliminary tests that when 0.0001M solutions of benzenediazonium chloride were poured into alkaline solutions either of R-salt or Schaeffer's salt the formation of the azo derivative was practically quantitative as determined by spectrophotometric comparison with a known amount of the pure dye. The sodium salt of 1-2-naphtholsulfonic acid[6] was selected, however, for more exact work as it reacts with diazo compounds in dilute solution much more readily and completely than most of the common sulfonated naphthol derivatives and can give only para azo dyes. It can be made and purified without special difficulty and does not undergo oxidation very rapidly when exposed in alkaline solution to the action of the air (an advantage over resorcinol). No direct comparative data were found relative to the azo dyes derived from this substance, but it was believed that as para derivaties of α-naphthol they would show greater tendency to vary in hue with varying hydrogen ion concentrations, a fact that would aid in their identification; and furthermore, that they would possess such solubilities that they might be conveniently separated from most other substances by the use of immiscible solvents. The monosodium salt

---

[1] *Ber.*, 1899, 32: 1691; 1900, 33: 527.
[2] *J. Chem. Soc.*, 1901, 81: 1412; 1903, 83: 220.
[3] *Ibid.*, 1907, 91: 35.
[4] *Ber.*, 1897, 30: 670.
[5] *Ibid.*, 1900, 33: 893.
[6] See Friedlaender and Taussig, *Ber.*, 1897, 30: 1457 for method of preparation. The salt may be purchased from the Eastman Kodak Co., Rochester, N. Y.

of 1-2-naphtholsulfonic acid is designated throughout this paper as sodium *a*-naphtholsulfonate.

DETERMINATION OF CONSTANTS.

The disodium salt of benzeneazo-naphthol sulfonic acid was prepared by mixing solutions of pure benzenediazonium chloride (made by Knoevenagel's method[1] with a quantity of sodium *a*-naphtholsulfonate slightly greater than the equivalent amount, and then adding a slight excess of sodium carbonate solution. The dye was separated by the careful addition of strong C. P. sodium chloride solution, the precipitate filtered on a Büchner funnel and the pressed cake washed with dilute sodium chloride solution and alcohol; dissolved in hot water, salted out and filtered as before. It was then washed successively with moderately strong salt solution, dilute salt solution, alcohol and ether, several rinsings or treatments with the alcohol and ether being given. This general process, used by the writer for ten years in the preparation of dyes free from appreciable amounts of inorganic impurities, possesses the advantage that the thoroughness of the purification may be judged after estimating the percentage of chlorides in the product.

The dyes derived from ortho-toluidine, para-toluidine, anthranilic acid, benzidine, *a*-naphthylamine and *b*-naphthylamine were prepared similarly, except that in the case of benzidine the base was diazotized in water solution and the diazo salt precipitated with alcohol[2]; and with the naphthylamines, the diazotizations were carefully made in water solution—avoiding excess of nitrite—and the diazo solutions used directly.

The dyes, as thus separated, were the disodium salts or phenolates, except those made from benzidine and methyl anthranilate which were the tetrasodium and monosodium derivatives, respectively. Attempts to prepare the dyes from aniline, the toluidines and the naphthylamines in the form of either the monosodium salts or free sulfonic acids were less successful, these substances separating in such form as to render their filtration extremely difficult. The dye from methyl anthranilate, however, was prepared as the monosodium salt, using sodium acetate in the coupling and carefully avoiding any excess of alkali or strong acid in the operations. Sulfanilic acid and naphthionic acid were diazotized in the usual way with an excess of nitrite, the diazo compounds washed and then added to an excess of the naphtholsulfonate. The subsequent treatment was the same as that given above, except that after the first washing the phenolate was decomposed by the addition of sufficient hydrochloric acid to neutralize the liquid, the colors being finally separated as the disodium salts. The hues of the solutions of these coloring

---

[1] *Ber.*, 1890, 23: 2994; 1895, 28: 2048.
[2] Castellaneta, *Ber.*, 1897, 30: 2800.

matters are shown in Table 1. Some of the dyes are almost insoluble in dilute acid or saline mixtures and hence are more or less completely precipitated when hydrochloric acid or the acetate buffer mixture is added to their aqueous solutions.

TABLE 1.

Hues of azo dyes derived from 1-2-naphtholsulfonic acid.

AMINE FROM WHICH DERIVED	APPEARANCE OF DYE	HUE OF 0.005% SOLUTION — SOLVENT: 0.1N Sodium Hydroxide	0.1N Hydrochloric Acid	Sodium Acetate-Acetic Acid Mixture*
Aniline	Red-brown powder	Orange	Orange-red	Orange-red
o-Toluidine	Brown cryst. powder	Yellow-orange	Red-orange	Red-orange
p-Toluidine	Red-brown cryst. powder	Orange	Orange-red	Orange-red
a-Naphthylamine	Brown cryst. powder	Orange-red	Dull green-yellow†	Dull red-brown†
b-Naphthylamine	Red-brown powder	Orange-red	Yellow-brown†	Violet-red†
Benzidine	Black powder	Violet-red	Dull red-violet†	Dull red-violet†
Anthranilic acid	Scarlet powder	Orange	Orange-red	Violet-red
Methyl anthranilate	Orange powder	Orange	Orange-red†	Orange-red†
Sulfanilic acid	Red powder	Red	Orange	Orange
Naphthionic acid	Black cryst. powder	Violet-red	Brown-orange	Brown-orange

*Solution containing in 1 liter 0.1 molecule of sodium acetate and 0.1 molecule of free acetic acid.
†Indefinite as part of the coloring matter was in suspension.

The percentages of moisture, total sodium and chlorine in the preparations were estimated by the official methods[1] and the amount of coloring matter calculated, correction being made for the small quantity of monosodium compound usually present. The solutions used for the optical examination were, in most cases, so prepared as to contain in one liter exactly 0.0500 gram of pure dye as disodium derivative. The dyes from the unsulfonated amines showed, excepting in the case of benzidine, values for the proportion of sodium from 0.3 to 0.5 per cent below that required by theory for the phenolate salt. The phenolic acidity of these substances is so weak that it is very difficult to wash them thoroughly on the filter without hydrolizing them to some extent. The benzidine derivative contained a considerable amount of the hydrolized compound formed during washing.

The dye from *b*-naphthylamine contained 1.53 per cent of sodium chloride. The other products, however, were free from amounts of this substance exceeding 0.3 per cent.

Dilute solutions of each of the dyes were tested with phosphate and

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 131.

borate buffer or regulator mixtures[1] to determine the hydrogen ion concentrations between the limits 10^{-5} and 10^{-9}, at which the maximum color change is produced by a given change in the hydrogen ion exponent. With the dyes from aniline, the toluidines, the naphthylamines, sulfanilic acid and naphthionic acid the maxima were at alkalinities corresponding to hydrogen ion concentrations between 10^{-7} and $10^{-8.2}$, and the hue at 10^{-9} was almost identical with that in 0.1N sodium hydroxide. It was assumed, therefore, that in so far as the effect of the hydrogen ion concentration was concerned, the optical properties of solutions in 0.1N sodium hydroxide and in normal sodium carbonate should be practically identical, and that the differences shown with ordinary mixtures containing equal quantities of carbonate and bicarbonate should be small[2].

The transmittances of solutions of the dyes were determined with the König-Martens spectrophotometer, quartz mercury lamp and double cell used for work already described[3], values being expressed as "extinction coefficients" or transmissive indices[4].

Table 2 shows the values found with 0.1N sodium hydroxide solutions containing in one liter an amount of the respective dye corresponding to 0.0500 gram of the pure disodium derivative, except in case of the methyl anthranilate derivative for which the pure color was calculated as the monosodium salt. Other solvents employed were 0.1N hydrochloric acid and 0.1N acetate mixture, the latter being a solution made by mixing one volume of normal sodium hydroxide with two volumes of normal acetic acid and diluting to ten volumes. Determinations were made also with several of the colors using normal (0.5M) and 0.5N sodium carbonate solutions as solvents, the values found in each case being very closely similar to those obtained with 0.1N sodium hydroxide. Satisfactory neutral and acid solutions of the colors from benzidine and the naphthylamines could not be prepared because of the low solubility of these dyes. The values for the derivatives of aniline and the toluidines obtained with hydrochloric acid and with the acetate mixture as solvents showed no differences so marked as to be well adapted for their differentiation. The observations were made at room temperature, which was 28°C. The figures given in Column 4 of Table 2, under the heading "Transmissive Index A", were calculated from those in Column 3 and express the transmissive indices for solutions containing in a liter

---

[1] Sörensen. *Biochem. Z.*, 1909, **21**: 175 and *Ergebnisse Physiol.*, 1912, **12**: 437, 438; Palitzsch. *Biochem. Z.*, 1915, **70**: 341; Clark & Lubs. *J. Biol. Chem.*, 1916, **25**: 501.

[2] Auerbach and Pick, *Arb. Kais. Gesundh.*, 1911, **38**: 256, give the value $10^{-9.9}$ for the hydrogen ion concentration at 18° C. of a solution made by mixing equal volumes of 0.05M sodium carbonate and 0.1M sodium acid carbonate.

[3] *J. Ind. Eng. Chem.*, 1920, **12**: 883.

[4] Priest, *J. Optical Soc. Amer.*, 1920, **4**: 186; Bunsen and Roscoe, *Pogg. Ann. Physik*, 1857, **101**:248, defined the extinction coefficient of an absorbing medium as the reciprocal of the thickness of the layer required to reduce the intensity of the incident light to 1/10 its original value. They pointed out also that with a dissolved colored substance this function could be taken as proportional to the concentration.

the quantity of the dye in question equivalent to 0.0100 gram of the corresponding amine.

TABLE 2.

Extinction coefficients or transmissive indices of azo derivatives of 1-2-naphthol-sulfonic acid in 0.1N sodium hydroxide solutions.

AMINE FROM WHICH DERIVED	WAVE LENGTH IN $\mu\mu$ OF LIGHT EMPLOYED	TRANSMISSIVE INDEX OBSERVED	TRANSMISSIVE INDEX A
Aniline	436	1.87	1.50
Aniline	546	0.89	0.71
Aniline	579	0.18	0.08
o-Toluidine	436	2.09	1.37
o-Toluidine	546	0.67	0.44
o-Toluidine	579	0.08	0.06
p-Toluidine	436	1.86	1.22
p-Toluidine	546	0.83	0.55
p-Toluidine	579	0.09	0.06
a-Naphthylamine	436	1.50	0.88
a-Naphthylamine	546	1.83	1.08
a-Naphthylamine	579	0.57	0.34
b-Naphthylamine	436	1.59	0.94
b-Naphthylamine	546	1.78	1.05
b-Naphthylamine	579	0.34	0.20
Benzidine	436	0.48	0.28
Benzidine	546	2.00	1.18
Benzidine	579	1.40	0.82
Anthranilic acid	436	2.15	1.23
Anthranilic acid	546	0.55	0.315
Anthranilic acid	579	0.04	0.025
Methyl anthranilate	436	1.55	0.84
Methyl anthranilate	546	1.40	0.75
Methyl anthranilate	579	. .	.
p-Sulfonilic acid	436	1.35	0.71
p-Sulfonilic acid	546	2.20	1.15
p-Sulfonilic acid	579	0.50	0.26
Naphthionic acid	436	1.04	0.47
Naphthionic acid	546	2.68	1.20
Naphthionic acid	579	1.45	0.65

The transmissive indices of the dye derived from methyl anthranilate in 0.1N sodium hydroxide solution could not be obtained directly because of the rapid saponification of the ester. The alkaline solutions were prepared by mixing such amounts of stronger aqueous solutions of the coloring matter, 5N sodium hydroxide solution and water as to give the desired concentration. Readings were then taken at definite intervals from the time of mixing in light of wave lengths $436_{\mu\mu}$ and $546_{\mu\mu}$

and the values for solutions of the pure ester calculated from these numbers. Measurements made at 546$\mu\mu$ with solutions in 0.1N sodium hydroxide containing 0.100 gram of pure color per liter gave the values shown below, the first readings being taken about four minutes after mixing. The temperature was kept at 20°C. ±0.3°C.

TABLE 3.

Transmissive indices of dyes from methyl anthranilate.

TIME IN MINUTES AFTER FIRST READING (t–t′)	TRANSMISSIVE INDEX AT 546 $\mu\mu$ (r)	VELOCITY CONSTANT (c)
0	2.57	.....
7	2.24	0.0151
14	1.99	0.0148
26	1.69	0.0143
41	1.43	0.0145
62	1.22	0.0150
95	1.09	0.0156
1300	1.04	......

The velocity constant (c) as given in Table 3 was calculated by the formula—

$$c = \frac{1}{t\text{-}t'} \text{ Log } \left(\frac{2.57 - 1.04}{r - 1.04}\right).$$

NOTE.—As the solution contained a large excess of alkali it was assumed that the amount of dye saponified at any instant was proportional to the amount of ester present at that time.

A few similar measurements at 40°C. gave the value 0.064 for the velocity constant at this temperature. The transmissive index at 546$\mu\mu$ of the anthranilic acid derivative at 40°C. appears to be approximately 2 per cent higher than at 20°C.

The monosodium salt of 4:1:2 nitroso-naphtholsulfonic acid was prepared by mixing solutions of equivalent amounts of sodium nitrite and sodium α-naphtholsulfonate and adding a slight excess of acetic acid. The reaction mixture was allowed to stand for several hours and the yellow crystalline nitroso compound then filtered off and purified by recrystallization, the salt being finally obtained in the form of bright yellow needles containing two molecules of water. Moisture was determined by drying at 125°C. to constant weight. The analyses gave the following results:

Moisture found—11.37 per cent (calculated 11.58 per cent).

Sodium found—7.36 per cent (calculated 7.39 per cent).

From these figures the transmissive indices were calculated for solutions in 0.1N sodium hydroxide containing in one liter the amount of

TABLE 4.

Values for the transmissive indices.

SOLVENT	WAVE LENGTH IN $\mu\mu$ OF LIGHT EMPLOYED	CONCENTRATION (Gram per liter)	TRANSMISSIVE INDEX OBSERVED
0.1N sodium hydroxide.......	436 546	0.0500 0.0500	1.64 0.035
0.1N hydrochloric acid ..	436 546	5.00 5.00	0.53 Less than 0.01
Solution containing in 1 liter 0.1 molecule of acetic acid and 0.1 molecule of sodium acetate............	436 546	2.50 2.50	0.39 Less than 0.01

dye corresponding respectively to one centigram of water-free sodium nitroso-naphtholsulfonate, one centigram of sodium nitrite and one centigram of nitrous acid. The values were as follows:

TABLE 5.

Transmissive indices of sodium nitroso-naphtholsulfonate.

WAVE LENGTH IN $\mu\mu$ OF LIGHT EMPLOYED	TRANSMISSIVE INDEX FOR DRY DYE	TRANSMISSIVE INDEX CORRESPONDING TO 0.01 GRAM OF SODIUM NITRITE	TRANSMISSIVE INDEX CORRESPONDING TO 0.01 GRAM OF NITROUS ACID
436 546	0.370 0.008	1.47 0.03	2.16 0.05

SPECTROPHOTOMETRIC ESTIMATION OF AMINES.

The data in Table 5 were applied for the estimation of amino compounds, the tests being made as follows: The solution of 0.00050–0.00100 gram of the base in 100 cc. of 0.25N hydrochloric acid was treated at room temperature (25°-30°C.) with 1.0 cc. of 0.5N sodium nitrite solution, stirred and allowed to stand exactly 2 minutes. It was then poured, with stirring, into a beaker containing a mixture of 15 cc. of 5N (2.5M) sodium carbonate solution and 5 cc. of a 5 per cent solution of sodium α-naphtholsulfonate. The solution was transferred to a graduated flask, diluted to exactly 150 cc. or 200 cc. and the transmittance determined at $546_{\mu\mu}$.

The colored solution obtained by this procedure contained in addition to the azo dye a small amount of the intensely yellow nitroso derivative of sodium α-naphtholsulfonate. The effect of this on the light absorption at $546_{\mu\mu}$ was negligible, however, as was shown by taking readings

at $436\mu\mu$ and calculating the correction. For example, 100 cc. of a solution of 0.00100 gram of carefully prepared crystallized sodium naphthionate was treated as described, the dye solution being finally diluted to 150 cc. The readings for the transmissive indices at $546\mu\mu$ and at $436\mu\mu$ were, respectively, 0.552 and 0.325—recovery, 97.5 per cent. A similar test using 0.00200 gram of naphthionate in 50 cc. of acid and finally diluting to 100 cc. gave indices at $546\mu\mu$ and $436\mu\mu$ of 1.656 and 0.881, respectively—recovery, 97.5 per cent. When quite accurate analytical results are desired it would seem necessary in all cases to carry through parallel determinations with known quantities of the pure amine to eliminate small errors such as those due to variation in temperature, alkalinity and salt content of the solutions.

A special case exists with the dye derived from diazotized methyl anthranilate since this coloring matter gradually saponifies in alkaline solution forming the anthranilic acid derivative, the absorption at $436\mu\mu$ increasing, that at $546\mu\mu$ decreasing. The velocity constant for the rate of saponification in 0.5M sodium carbonate solution at 30°C. was found to be approximately 0.0027, from which it follows that during the first minute after mixing the reading at $546\mu\mu$ had decreased about 1/300 of its value. With such solutions the change in the transmission for a time interval of, say five minutes, will be very small and almost the same as that taking place during the next equal interval.

The following equation is calculated from the data already given and shows the amount of the amine corresponding to the total coloring matter in a solution in 0.1N sodium hydroxide containing both saponified and unsaponified dye, X representing the quantity of total amine (in centigrams per liter), a and b the respective transmissive indices of the solution at $436\mu\mu$ and $546\mu\mu$ at any given instant: $X = 0.773\ a + 0.465\ b$. This formula is of interest but is not strictly applicable under conditions easily fixed in analytical practice.

The general procedure for the coupling of the diazo compounds that has just been discussed is open to two disadvantages. With the simpler derivatives such as those from aniline and the toluidines the absorptions at $546\mu\mu$ are rather low. The radiation of wave length $492\mu\mu$ from the mercury arc would be much more suitable but, like similar monochromatic light from other sources, is not intense enough for spectrophotometric work with the König-Martens apparatus. Furthermore, the dyes are obtained in alkaline mixtures containing sodium nitrite and sodium α-naphtholsulfonate, and can not be conveniently separated from these substances with immiscible solvents. To insure complete diazotization before any appreciable quantity of the diazo compound has suffered decomposition, an amount of nitrite equal perhaps to 0.0005 molecule of nitrite has been employed to diazotize 0.00001 molecule of amine. If the carbonate solution is acidified, the nitrous acid at once reacts with

the sodium *a*-naphtholsulfonate, producing an amount of new coloring matter very much greater than the quantity of azo dye present and forming a mixture from which the latter can scarcely be separated satisfactorily.

Experiments were made with a number of amines using hydrazine sulfate to destroy the excess of nitrous acid before coupling. According to Dennstead and Gohlich[1] the products formed by the action of hydrazine sulfate on nitrous acid are water, nitrogen, oxygen, nitrous oxide, sulfuric acid and azoimid or triazoic acid. The reaction of diazo compounds with hydrazine and with azoimid has been investigated by Noelting and Michel[2] who showed that in both cases the diazo salts were converted under the conditions of their experiments into the corresponding organic azoimides. The common organic azoimides are not strongly colored and are moderately stable so that their formation in small amount is without perceptible influence on the colorimetric procedure excepting in so far as destruction or loss of the diazo compounds is involved.

Tests were made with several different amines according to the following procedure:

The solution of 0.00100 gram of the amine in 100 cc. of 0.25N hydrochloric acid was treated at room temperature (28°C.) with 1.0 cc. of 0.5N sodium nitrite and allowed to stand exactly 2 minutes. Four cc. of a 3% solution of hydrazine sulfate was added and the mixture well stirred for 20 seconds. About 5 cc. of the 5% solution of sodium *a*-naphtholsulfonate was then poured in, followed quickly by 15 cc. of 5N (2.5M) sodium carbonate. The portions of *a*-naphtholsulfonate and sodium carbonate were previously measured off in graduated cylinders so that they could be added to the diazo solution and mixed quickly. In case of the carbonate solution special care was taken to pour it into the solution in such a way that the full addition and mixture were made almost instantly.

When solutions of *b*-naphthylamine were treated by this procedure 97% or more of the amine was converted into the dye. The coloring matter was estimated directly in the mixture after diluting it to a known volume; it was also estimated in other tests by acidifying the liquid and extracting the dye with 3 small portions of amyl alcohol. The latter was washed with 0.1N hydrochloric acid, diluted with petroleum ether, the dye extracted with 0.1N sodium hydroxide and the solution made to a definite volume in the same solvent. Aniline and methyl anthranilate gave yields of 93–95% of the corresponding dyes. The yield from naphthionic acid was variable and lower (70–80%).

Similar experiments with aniline using Schaeffer's salt and R-salt instead of the sodium *a*-naphtholsulfonate showed that with these *b*-naphthol derivatives less than one-third of the diazo compound was converted into dye. This would seem clearly to be due to the lower velocity of the coupling of the *b*-naphthol derivatives as the result of which more of the diazo compound reacted with the hydrazine.

The procedure with hydrazine sulfate is convenient and when check

[1] *Chem. Ztg.*, 1897, 21: 876. See also Curtius, *Ber.*, 1893, 26: 1263.
[2] *Ber.*, 1893, 26: 86.

determinations with known amounts of amine were carried through at the same time and in exactly the same way gave fairly accurate data in most cases. In order to limit the side reactions as much as possible it was found desirable to use but a little more hydrazine sulfate than was necessary to destroy the nitrous acid completely. A few blank tests made by treating 100 cc. portions of 0.25N hydrochloric acid with sodium nitrite, hydrazine sulfate, sodium *a*-naphtholsulfonate and sodium carbonate served to show the quantity of the hydrazine sulfate solution which under the conditions was just sufficient to prevent the formation of yellow coloring matter when the liquid was made alkaline. An excess of 0.5 to 1 cc. of the approximately 3 per cent solution was used in the test with amines.

The intense coloring power of sodium nitroso-naphtholsulfonate, and the ease with which it is formed from sodium *a*-naphtholsulfonate suggested that the latter substance might serve as a useful reagent for the spectrophotometric estimation of nitrous acid. Ten cc. of a 0.00100M solution of sodium nitrite were mixed with 2 cc. of 5 per cent sodium *a*-naphtholsulfonate solution, cooled to about 8°C. and acidified with 0.10 cc. of 5N hydrochloric acid. After standing for ten minutes the mixture was made alkaline with 2.1 cc. of 5N sodium hydroxide, diluted to 100 cc. and the transmissive index at $436_{\mu\mu}$ determined. The value found was about 96 per cent of that calculated from Table 5. The standard dilute sodium nitrite solution was prepared from crystallized silver nitrite and sodium chloride, and it is possible that a slight change in titre through absorption of oxygen may have taken place during its preparation. The *a*-naphtholsulfonate does not react with nitrates in these dilute solutions.

COLORIMETRIC METHOD FOR THE ESTIMATION OF *B*-NAPHTHYLAMINE IN COMMERCIAL OIL-SOLUBLE FOOD DYES.

The colorimetric method outlined below has been used for the estimation of small amounts of *b*-naphthylamine in samples of commercial Yellow A B (benzeneazo-*b*-naphthylamine) and Yellow O B (*o*-tolueneazo-b-naphthylamine). Since the proportion of *b*-naphthylamine in these products seldom exceeds 0.5 per cent a method giving figures accurate to about 10 per cent of their value is considered satisfactory.

Separation of b-naphthylamine from Yellow A B and Yellow O B.

The *b*-naphthylamine is separated by dissolving 1.00 gram of the dye in 50 cc. of benzene and extracting in a separatory funnel with four 25 cc. portions of 0.25N hydrochloric acid. A second funnel containing 50 cc. of benzene is provided and the acid portions separately shaken out with this solvent, being passed through the second funnel in the same order as through the first. With some commercial dyes the impurities form a precipitate that appears at the junction of the two liquid layers in the first funnel and interferes with their complete separation. The precipitate may usually

be caused to collect so as to occupy a volume not greater than 2–4 cc. by gently rotating the funnel. However, only the clear solution should be drawn into the second funnel and as the separation of the acid is thus incomplete it is necessary in such a case to pass an additional washing portion of acid through the funnels and test it to make sure that all naphthylamine has been extracted.

Conversion of base into azo dye.

The solution of the base in about 100 cc. of 0.25N hydrochloric acid is treated at room temperature (20°–30°C.) with 1 cc. of 0.5N sodium nitrite solution and allowed to stand exactly two minutes. 5 cc. of a saturated solution of hydrazine sulfate is added, the mixture stirred, allowed to stand exactly ½ minute and treated with 5 cc. of a 5% solution of sodium *a*-naphthol-2-sulfonate and finally with 15 cc. of a 25% solution of sodium carbonate. The sodium carbonate must not be poured in slowly but should be added in one portion and the solutions quickly mixed by stirring. The alkaline dye solution is finally diluted to 200 cc. A solution containing a known amount of *b*-naphthylamine is carried through in exactly the same way and aliquot portions of the two dye solutions obtained are diluted further if necessary, and compared colorimetrically. If the results show the standard to be very dissimilar in concentration to the solution under examination it is discarded and a more similar standard prepared. The comparison is best made in monochromatic green, blue or violet light. If a white light source is used a colored glass or film should be placed in the path of the light to intercept the red, orange and yellow rays.

NOTE.—Care must be taken that no appreciable amount of the mixture adhering to the walls of the beaker above the surface of the liquid escapes the action of the hydrazine and that the diazo solution is not exposed to brilliant sunlight.

Procedure with dyes contaminated with a-naphthylamine derivatives.

A sample of Yellow A B contaminated with benzeneazo-*a*-naphthylamine will give a reddish acid extract when treated as described above. The amount of this base removed is usually very small, but its influence on the colorimetric determination of the naphthylamine may be eliminated when necessary as follows: The pink acid extract containing the naphthylamine is compared before the diazotization-coupling operation with a somewhat more strongly colored solution of benzeneazo-*a*-naphthylamine in 0.25N hydrochloric acid and the latter then diluted with 0.25N acid until the color concentration is the same. 100 cc. of this solution is carried through the diazotization and coupling processes in exactly the same way as the dye extract and the standard naphthylamine solutions. 20 cc. of the resulting solution (containing sodium benzeneazo-naphthaleneazo-naphtholsulfonate) is placed in a graduated 100 cc. colorimetric tube and 20 cc. of the dye solution obtained from the acid extract is measured into a second similar cylinder. The dye solution from the standard naphthylamine mixture is then added to the first cylinder from a buret until the liquids show nearly the same color on looking down the tubes. They are finally diluted to the equal volumes and a few drops more of the standard naphthylamine dye solution added to the known mixture to bring its color intensity exactly to that of the sample. The buret reading divided by 20 and multiplied by the weight of *b*-naphthylamine used in making the standard solution gives the amount of *b*-naphthylamine in the original unknown solution.

Application of the method with dyes containing aniline or o-toluidine.

Aniline and o-toluidine do not often occur as impurities in Yellow A B and Yellow O B. When present, they are extracted with the *b*-naphthylamine in the treatment with benzene and produce the corresponding azo derivatives in the coupling process. Dilute alkaline solutions of these derivatives are orange in hue, while a similar solution

of the *b*-naphthylamine derivative is red. The amounts of each of the components in a mixture of two dyes of dissimilar hue, while best determined with the spectrophotometer, may be judged by colorimetric comparisons with known mixtures.

SUMMARY.

1. Values are given for the transmissive indices or extinction coefficients of alkaline solutions of the azo dyes formed from aniline, *o*-toluidine, *p*-toluidine, *a*-naphthylamine, *b*-naphthylamine, benzidine, anthranilic acid, methyl anthranilate, sulfanilic acid and naphthionic acid by diazotizing and coupling with 1-2-naphtholsulfonic acid.

2. Similar values are given for the transmissive indices of solutions of 4:1:2 nitroso-naphtholsulfonic acid.

3. The application of these values to the estimation of small amounts of the amines is discussed.

4. Tests are described in which the sodium salt of 1-2-naphtholsulfonic acid was used as a reagent for the estimation of nitrites.

5. A method is described for the colorimetric estimation of *b*-naphthylamine in commercial oil-soluble food colors.

REPORT ON METALS IN FOODS.

By W. F. Clarke (Bureau of Chemistry, Washington, D. C.), *Referee.*

The work of the referee for 1920 was limited to the devising of a modification of the Penniman method[1] for tin and to a collaborative study of the modification. The resulting revision carries several features of the Baker-Sellars method[2].

Briefly, the original Penniman method may be outlined as follows:

The tin is separated from the food material by extraction with hydrochloric acid and filtration of the acid solution; after adjustment of the acid concentration powdered zinc is added to the hydrochloric acid extract to precipitate the tin; after filtration the mixed metals are dissolved in hydrochloric acid in an atmosphere of carbon dioxide; after cooling in the same atmosphere the stannous chloride is titrated with potassium iodate.

Objections to the original method are based on these points:

(1) Some of the coloring matter extracted by the hydrochloric acid may be carried along throughout the process and may interfere when the stannous chloride is being titrated.

(2) It appears that the zinc does not completely precipitate the tin; possibly it might do so were the proportions of zinc and acid varied considerably from those proposed in the original specifications.

---

[1] *J. Assoc. Official Agr. Chemists*, 1920, **4**: 175.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 150.

(3) The titration of stannous chloride with potassium iodate in the presence of strong hydrochloric acid involves at least four reactions. It was assumed that the stannous chloride is completely oxidized before the remaining three reactions begin, the end point being marked by the liberation of free iodine due to one of the later reactions. It has been found, however, that iodine is liberated prior to the complete oxidation of the stannous chloride.

After modification of the method based upon these criticisms, your referee sent out samples and directions for collaborative study. An outline of the specifications submitted is as follows:

Destroy the organic matter by wet combustion in a Kjeldahl flask; transfer the residue, consisting in part of metastannic acid and stannic sulfate, to a large Erlenmeyer flask, the Kjeldahl flask being washed out with hot sodium hydroxide solution. Make the liquid in the Erlenmeyer suitably acid with sulfuric acid and precipitate the tin as metal by means of an initial charge of powdered zinc and a later charge of powdered iron. After decantation through an asbestos mat, washing to remove sulfates, dissolve the metals in hydrochloric acid, an atmosphere of carbon dioxide being maintained during the dissolving and the later cooling. Titrate the resulting stannous chloride with 0.01N iodine which has been standardized by thiosulfate, the value of which is determined by running against weighed dry iodine.

The samples sent out consisted of a solution of tin chloride, some tin foil and a supply of tin-free dried beans.

To 20-gram portions of the beans in a Kjeldahl flask each analyst added a measured portion of the tin solution or a weighed amount of tin foil.

The results obtained are shown in the table, page 30.

In explanation of the large amounts of tin apparently found in the blanks it will be noted that the values are the same for blanks with beans and for those without beans; in other words, the beans are tin-free. Furthermore, the work of Hale[1] has shown that for very dilute iodine a large blank is found when the volume of solution is large and the concentration of potassium iodide is low. This effect is increased under the conditions reported here with the result that for quantities of tin of at least 5 milligrams the amount apparently found is excessive; however, when 10 milligrams or more are present the volume of iodine required contains enough potassium iodide to eliminate this error. Some unreported determinations were run, in which an effort was made to add potassium iodide solution in sufficient amount, but it was found that free iodine was liberated under the conditions of the method. Further work will be done on that point. Finally, it appears that for an amount of tin of 10 milligrams or more the titration with iodine gives a reasonably good figure, the blank being disregarded.

[1] *Am. Chem. J.*, 1902, **28**: 450.

ANALYST	SAMPLE OF BEANS	TIN PRESENT	TIN FOUND
	grams	*milligrams*	*milligrams*
A. E. Stevenson, National Canners Association, Washington, D. C.	0	0	0.24
	0	0	0.21
	20	0	0.36
	20	0	0.42
	20	5.00	4.04
	20	5.00	4.39
	20	50.00	48.19
	20	50.00	43.38
	20	5.63	5.10
	20	5.63	5.34
	20	22.50	21.54
	20	22.50	21.60
	20	56.25	52.88
	20	56.25	52.17
R. M. Hann, Bureau of Chemistry, Washington, D. C.	20	0	1.20
	20	5.63	7.08
	20	56.25	56.13
	20	56.25	55.78
	50	33.75	34.48
	0	11.25	11.14
	0	11.25	11.23
	0	11.25	11.69
W. F. Clarke.	0	0	1.03
	0	0	1.36
	20	0	1.09
	20	0	1.31
	20	5.63	5.91
	20	5.63	6.49
	20	22.50	22.61
	20	22.50	22.66
	20	56.25	55.87
	20	56.25	56.37
	20	4.71	5.40
	20	5.50	6.36
	20	33.96	33.76
	20	25.70	25.44

The only comment received was from Hann, who considers the proposed modification an improvement over the original Penniman method and also over the Baker-Sellars method. He states that it avoids both the laborious filtration of the metals in the original method and the precipitation and subsequent dissolving of sulfide as required in the Baker-Sellars method. He also reports that results are more consistent than those found by the other methods.

DISCUSSION.

The analysts' results are better than those found last year when the original method was studied. The accuracy is about equivalent to that of a carefully performed Baker-Sellars procedure. Apparently the

wet combustion is slower than the hydrochloric acid extraction in the original method, but in reality it takes much less of the analyst's time; besides it avoids the carrying along of interfering coloring matter. The precipitation of the sulfide in the Baker-Sellars method and its more disagreeable subsequent dissolving are substituted for the Penniman zinc precipitation procedure, which is made complete by a later charge of powdered iron, the effectiveness of which is probably due to a coupling effect with the other metals. An interesting controversy is now in progress between Kolthoff and Bouman[1] regarding the procedure of Ada Prins[2] in precipitating tin by powdered iron. The inaccurate iodate titration of the original method is replaced by the use of iodine.

RECOMMENDATION.

It is recommended that the modification of the Penniman method for tin be studied further with collaborative work.

REPORT ON ARSENIC IN FOODS.

By R. M. Hann (Bureau of Chemistry, Washington, D. C.). *Associate Referee.*

In accordance with the recommendation of the Referee on Metals in Foods, 1920, the H. V. Farr modification of the Gutzeit method was subjected to a comparative study with the present tentative Gutzeit method[3].

APPARATUS

The modified apparatus consists of a generator equipped with a funnel, for the introduction of acid and reagents, and an outlet tube, through which the gases evolved are passed before contact with the sensitized paper. The generator itself is cylindrical in shape, of approximately 50 cc. capacity and has a hollowed ground-glass stopper to allow placement of the other parts of the apparatus without overcrowding and general instability. The funnel is introduced through the top; its stem is placed as near the center of the generator as possible and reaches nearly to its base. The outlet is a small calcium chloride tube in which the gases are purified by contact with lead acetate cotton and diffused before final passage through the mercuric chloride paper attached to its extremity. The apparatus is of glass and ground joints are used throughout

REAGENTS.

The reagents required are arsenic-free zinc (No. 30-mesh powder), arsenic-free hydrochloric acid, saturated water solution of bromine and a 10% solution of potassium iodide. The sensitized paper was prepared by soaking soft filter paper in 5% mercuric chloride solution and spreading it on a clean towel until dry.

[1] *Rec. trav. chim.*, 1920, **39**: 537–41, 606–8, 711–14.
[2] Prins, Ada. Beknopte leidraad voor qualitatieve chemische analyse, 1919 *Chem. Weekblad*, 1919, **16**: 1592.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 147

DETERMINATION.

Introduce 5 grams of the sample into the body of the apparatus and add 4 or 5 grams of No. 30 powder arsenic-free zinc. After inserting the stopper, add 6–8 drops of saturated bromine solution and then concentrated hydrochloric acid until fairly vigorous action commences. A very slight excess of bromine should be present at this time. Next fill the apparatus about ⅜ full with diluted hydrochloric acid. In 2–5 minutes add 10 drops of 10% potassium iodide solution and fill the apparatus to within ½ in. of the top with diluted hydrochloric acid. The strength of acid should be such that when a blank is run it will require from 30 to 40 minutes to dissolve the 4 grams of zinc. When practically all the zinc has dissolved remove the sensitized paper and estimate the arsenic by comparing the intensity of the stain with a set of standards prepared under like conditions with known amounts of arsenic.

A copy of the method, a set of apparatus, paper to be sensitized and a solution containing 350 milligrams of arsenious oxide per 100 cc., with directions for diluting the solution to a strength of 3.5 micromilligrams per cc., were sent to each of six collaborators, located at stations where arsenic work is part of the regular analytical procedure. The author of the method very kindly consented to assist and give the benefit of his experience.

The following results (reported in milligrams of arsenious oxide per kilo) were received from the collaborators:

Analyst	Tentative Gutzeit Method	H. V. Farr Modification
E. H. Berry, Food and Drug Inspection Station, Chicago, Ill.	5	4.5
J. O. Clarke, Food and Drug Inspection Station, Savannah, Ga.	...	3.0
R. Hertwig, Food and Drug Inspection Station, San Francisco, Calif.	...	3.0
	...	3.4
W. E. Kirby, Food and Drug Inspection Station, New York, N. Y.	3.6	3.4
	...	3.6
R. M. Hann	3.7	3.6
	...	3.5

COMMENTS BY COLLABORATORS.

J. O. Clarke.—Binding the sensitized paper over the end of the tube is a very excellent departure from the usual method of collecting the stain on a strip of paper. In my opinion this could be combined successfully with the present tentative method as outlined in the A. O. A. C. methods[1]. In other words, an ideal procedure appears to be the use of the reacting mixture as outlined in the present tentative method and the making of the stain as outlined in your method.

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 147.

W. E. Kirby.—In regard to changes suggested in the present tentative method for arsenic, I believe that the use of potassium iodide and warming the solution to 90°C. is unnecessary.

E. H. Berry.—Considerable difficulty was experienced with the Farr method. A large number of determinations were made where few, if any, stains were obtained. It was impossible to account for this as the details of the method were followed very closely. A special and delicate piece of apparatus is very objectionable. It is easily broken and it is believed the use of such an apparatus should be avoided, if possible, for a determination so frequently encountered as the arsenic determination. Again it does not seem possible to make as close a comparison of the stain spots on the paper, as it is of stain strips as obtained in the A. O. A. C. method. The directions for the A. O. A. C. method call for the use of 15 grams of stick zinc. It is believed that the use of so large an amount of zinc is unnecessary. The rapidity of the action in the generator bottle can be much more easily controlled with a much smaller amount of zinc. I would suggest that a further study of both methods be made.

R. Hertwig.—The tentative Gutzeit method of throwing the stains out into lengths has the extra advantage of having the length besides the intensity to aid in making comparisons. The technique of the official Gutzeit method is as simple as that of the Farr method. From my experience with the former, I should recommend it as having more in its favor as a practical working method and offering greater chances for reliable results than the method here under discussion.

DISCUSSION.

The work of the referee has almost entirely consisted of a study of the Farr modification. Excellent results were obtained in concentrations below twenty micromilligrams of arsenious oxide. Above this concentration perfect stains were consistently obtained but the accurate comparison of differences in color became difficult. Fading out of stains was not so noticeable, as observed by Clarke, and this objection will in all probability be overcome by the substitution of mercuric bromide for the chloride. While the preliminary treatment suggested seems adequate in the case of a simple arsenic solution it would doubtless be necessary to use a more vigorous method of reduction in the case of refractory substances. Samples of phosphoric acid were analyzed and they gave excellent checks with similar samples analyzed by the tentative method. The Farr method as it stands is admirably suited for rapid determination of arsenic when the amount of arsenic detected is below some definite limit, which at present is in the neighborhood of twenty parts per million. Renewed interest in the arsenic work is evident in the reports of the various collaborators. The objections to the Farr method are well founded, but in view of the promising results obtained by a majority of the collaborators, the method seems worthy of further study and possible modification. Several helpful suggestions were received, and an attempt will be made to determine the practicability of incorporating one or more of these ideas into the method as it now stands. The use of a larger outlet tube and therefore larger absorption surface, as suggested by Clarke, would tend to give a more

uniform stain but the difference in intensity of the stain per unit surface of the absorbing paper would be very slight and for that reason decrease the sensibility of the method. After working with the Farr modification, Clarke devised a simpler form of apparatus which he used with good results. An effort will be made to try out this apparatus.

Further study of the tentative method especially in regard to the potassium iodide reduction seems to be necessary. While the work of H. M. Loomis[1] and E. L. P. Treuthardt[2], former associate referees on arsenic, seems to prove the reduction with iodide an essential step there is a feeling among workers in this field that it is an unnecessary detail. In this connection it may be noted that the function of stannous chloride in the determination is almost entirely that of an accelerator and that it is doubtful if it acts as a reducing agent under the conditions. The work of the coming year will include a study of the value of this reduction.

RECOMMENDATIONS.

It is recommended—

(1) That the H. V. Farr modification of the Gutzeit method for the determination of arsenic be further studied with a view to simplifying the apparatus as described and ascertaining the conditions necessary for a more accurate determination in concentrations above 20 micromilligrams of arsenious oxide.

(2) That the present tentative Gutzeit method be studied again in comparison with the H. V. Farr modification.

REPORT ON DETERMINATION OF PECTIN IN FRUIT AND FRUIT PRODUCTS.

By H. J. WICHMANN[3] (U. S. Food and Drug Inspection Station, Denver, Colo.), *Referee.*

Fruits contain more or less natural pectin. The commercial pectin on the market at the present time is extracted from apple pomace, from dried apple chops, or from dried skins and cores from which the sugars and other substances soluble in cold water have been removed. This pectin can be legitimately used in those jams or jellies which are made from fruits low in natural pectin or those sensitive to continued boiling, provided its use does not conceal inferiority; for example, a deficiency of fruit. It is, therefore, of great importance to devise methods suitable for the purpose of detecting added commercial pectin and to determine whether it conceals inferiority due to a deficiency of fruit.

The Denver Station of the Bureau of Chemistry has developed

[1] *J. Assoc. Official Agr. Chemists*, 1915, 1: 244.
[2] *Ibid.*, 1916, 1: 580.
[3] Presented by W. W. Randall.

certain methods that appear to be useful for the purpose mentioned. It was determined to try out certain of these methods cooperatively.

Pectin is a constituent of the cell-wall of fruits and other plants soluble in water and insoluble in alcohol. The alcohol precipitate should, therefore, be a measure of the amount of pectin present in a fruit product. Accordingly, four methods for its determination were submitted to the collaborators.

Since gums, dextrine and other alcohol-insoluble substances, naturally or otherwise present in a jam or jelly, may contaminate the alcohol precipitate, or the nature of the fruit used or its degree of ripeness may cause variations in results, it was desired to obtain some derivative of pectin in a pure condition that would be a stable, definite chemical compound. "Pectic acid", formed by the action of alkali on pectin and subsequent precipitation with hydrochloric acid, was believed to be such a product. The method for pectic acid devised by the referee was therefore included in the list of methods sent to collaborators. It is not the purpose of this report to go into the chemistry of pectin or pectic acid, since it would lead too far afield.

One sample of strawberry jam containing added pectin was prepared by the referee, and portions were submitted to six stations of the Bureau of Chemistry for analysis. Reports from four of these stations were received. The formula employed in the preparation of the jam was as follows:

	POUNDS
Fruit	2.25
Commercial pectin	1.75
Sugar	11.50
Water	4.50
Total	20.00

The mixture was boiled until the temperature rose from 94° to 100°C. The total weight of the finished jam was 15 pounds, 11 ounces. The percentages of fruit and pectin in the finished jam, therefore, amounted to 14.3 and 11.1, respectively. In order to preserve the jam, it was well stirred while hot, transferred to fruit jars and sterilized by placing in boiling water for 20 minutes. A portion of the pulped strawberries used in the preparation of the jam was also sterilized in glass jars for analysis by the referee, for the purpose of comparing the jam and the fruit used in its preparation. Collaborators were requested to report results obtained according to the following outline:

METHODS.

PREPARATION OF SAMPLE.

The fruit should be pulped and the sample thoroughly mixed. This may be done by passing it through a meat chopper. Weigh 300 grams of the mixed sample into a 1.3

liter beaker, add 800 cc. of water, bring to a boil and boil for one-half hour. Transfer the jam solution to a 2000 cc. graduated flask, cool and make up to the mark. Filter through a folded filter. Make the following determinations on the filtrate except when otherwise directed:

NOTE.—Subsequent work by the referee indicates that the one-half hour boiling may not be sufficient in all cases. It was found that slightly increased amounts of pectin could be extracted from fruits by boiling from 1 to 2 hours. In the case of jams containing only 10 to 15 per cent of fruit, boiling for one-half hour is sufficient, but 50 per cent fruit jams may require a longer period. Therefore the referee recommends that the period of boiling be specified as 1 hour in all cases.

Alcohol Precipitate.

Method I.—Evaporate 100 cc. of the filtrate to 20 cc. and proceed exactly as indicated in the official and tentative method[1].

Method II.—Evaporate 100 cc. of the filtrate to 20 cc. If an insoluble scum forms during the evaporation, stir the cold solution vigorously and add 1 cc. of 10 per cent hydrochloric acid. This procedure will usually redissolve the insoluble substance. Add slowly from a separatory funnel, and with constant stirring, 200 cc. of 95 per cent alcohol. Allow the mixture to stand 1 hour. Standing overnight does no harm. Filter on a smooth, qualitative filter paper and wash the precipitate with 80 per cent alcohol. Wash the precipitate from the filter paper back into the original beaker with hot water. Wash the paper well. If insoluble substances were present before the addition of the alcohol, dissolve the precipitate on the paper and filter through the paper. Evaporate the water solution of the pectin to 15 cc., add 5 cc. of 10 per cent hydrochloric acid and again precipitate with alcohol as before. Allow the mixture to stand 1 hour, filter and wash well with 80 per cent alcohol. Now wash the precipitate from the filter into a platinum dish, evaporate to dryness, dry in a water oven for 1 hour, weigh and ash. Calculate the loss in weight as alcohol precipitate. The result of the second precipitation may be almost colorless. Care should be used to avoid loss in washing from the filter paper.

Method III.—Proceed as in Method II for the first precipitation. Previous to the second precipitation add 5 cc. of 10 per cent hydrochloric acid and one-half gram of acid-treated, ignited asbestos. Precipitate with alcohol the second time, allow to stand 1 hour and collect the alcohol precipitate and asbestos in a Gooch crucible with a thin asbestos mat. Wash with 80 per cent alcohol, suck dry and dry the crucible and contents in a water oven. Weigh, ignite and weigh again. The loss in weight is the alcohol precipitate.

Method IV.—Proceed as in Method II but make three precipitations of the alcohol precipitate. Omit the acid on the third precipitation.

Pectic Acid.

Evaporate 200 cc. of the jam solution to 25 cc. Precipitate with 200 cc. of 95 per cent alcohol. Allow to settle, filter and wash with 80 per cent alcohol. Dissolve the precipitate from the filter with hot water and wash well. Evaporate to 25 cc., cool and add 2 cc. of 10 per cent sodium hydroxide diluted to 25 cc. Allow to stand 15 minutes; then add 40 cc. of water and 10 cc. of 10 per cent hydrochloric acid and boil 5 minutes. Collect the pectic acid on a qualitative filter and wash with hot water. Wash the pectic acid back into the beaker with a stream of hot water. Adjust to 25 cc. and repeat the saponification and precipitation just described. Then wash the pectic acid into a platinum dish, evaporate to dryness, dry 1 hour in a water oven, weigh and ignite. The difference in weight is the pectic acid.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 156.

Ash.

Evaporate 100 cc. of the jam filtrate to dryness and ash at low redness. Determine water-insoluble and water-soluble ash, water-insoluble and water-soluble phosphoric acid, expressed as P_2O_5, by the official methods[1].

Sulfur in Ash.

Ash 100 cc. of the jam filtrate. Dissolve the ash in 5 cc. of 10 per cent hydrochloric acid and evaporate to dryness. Heat to 110°C. for an hour to dehydrate any possible silica. Add 5 cc. of 10 per cent hydrochloric acid and filter. Wash the filter paper with hot water. Precipitate the sulfur as barium sulfate from the boiling solution. Evaporate to 100 cc. and allow to stand overnight. Since the weight of the barium sulfate is very small a Monroe crucible would be convenient for collecting the precipitate.

Total Sulfur.

Into the largest casserole that can be placed in an available electric muffle, put 4 grams of magnesium oxide. Add 50 cc. of concentrated nitric acid and then 100 cc. of jam solution. Cover the casserole with a glass triangle and cover glass, and evaporate on the steam bath to a pasty consistency. Wash down the cover glass and triangle with water and again evaporate to a paste. Place the casserole in a cold electric muffle and gradually heat to low redness, until all nitrogen tetroxide fumes have been driven off. All the organic matter will have been destroyed. Then cool, dissolve in hydrochloric acid and filter. Adjust the acidity so that the solution contains 0.5 to 1 gram of free hydrochloric acid and precipitate the sulfate as barium sulfate from the boiling solution. Evaporate to approximately 100 cc. and allow to stand overnight. Do not evaporate to such an extent that salts will crystallize out. Filter, wash, ignite and weigh as usual. If possible, filter on a Monroe crucible. This determination should be made in a room free from sulfur fumes of all kinds. A careful blank should also be run with 2 quantitative filter papers as a source of organic matter. So-called C. P. magnesium oxide frequently contains considerable amounts of sulfur compounds.

Water-Insoluble Solids.

Method I.—Dry 15 cm. qualitative filter papers in covered aluminum dishes. Weigh 25 grams of mixed jam into a 400 cc. beaker. Add 200 cc. of water and boil gently for 30 minutes. Filter on the filter paper. If the paper becomes clogged, so that the filtering is too slow, it is better to start afresh with a smaller sample. Wash the insoluble solids well with hot water. When the washings are colorless or contain no acid, place filter and contents in the aluminum dish, dry and weigh. The difference in weight is the water-insoluble solids.

Method II.—Weigh into a 250 cc. beaker, 25 grams of the well-mixed product. Add 100 cc. of warm water and heat on the water bath for about an hour with frequent stirring. Place a fair-sized wad of absorbent cotton, previously dried in an aluminum dish and weighed, in a funnel, part of the cotton being wedged into the neck with a wire. Filter the fruit solution through this cotton. Wash with hot water until the wash water is no longer acid. Washing can be accomplished with approximately 250 cc. of water. Then replace the cotton wad, together with the insoluble fruit solids, in the aluminum dish, dry and weigh.

RESULTS.

The data obtained by the collaborators are collected in the following table and, in addition, the referee's results of analysis of the strawberry

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 105, 194.

Results of analysis of strawberry jam and strawberries.*

ANALYST	ASH	WATER-INSOLUBLE ASH	WATER-SOLUBLE PHOSPHOROUS PENTOXIDE	WATER-INSOLUBLE PHOSPHOROUS PENTOXIDE	ALCOHOL PRECIPITATE				PECTIC ACID	WATER-INSOLUBLE SOLIDS		SULFUR IN ASH	TOTAL SULFUR
					Method 1	Method 2	Method 3	Method 4		Method 1	Method 2		
Strawberry jam													
	per cent	*per cent*	*mgs. per 100 grams*	*mgs. per 100 g'ms*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*mgs. per 100 g'ms*	*mgs. per 100 g'ms*
H. J. Wichmann..............	0.185	0.053	trace	11.6	0.49	0.402 0.396 0.423	0.395 0.392	0.416 0.415 0.390	0.232 0.229 0.225	0.55	0.60	4.0	7.8
C. S. Brinton, Philadelphia†....	0.188	0.040	3.55 2.42	10.3	0.49	0.395	0.395	0.393	0.219 0.221	0.69 0.61	0.50 0.60	2.7	10.9
H. I. Macomber, Chicago†.....	0.21	0.035	3.0	12.0	0.47 0.46	0.41 0.42	0.36 0.36	0.35 0.38	0.19 0.19	0.75 0.72	0.72 0.69	3.6	57.0‡
D. B. Bisbee, St. Louis†.......	0.186	0.046	none	12.0	0.50 0.52	0.40 0.40	0.366 0.366	0.393 0.393	0.193 0.193	....	....	8.8	....
Strawberries													
H. J. Wichmann........ ...	0.59	0.17	7.2	51.3	....	0.690	0.632	0.641	0.433	3.88	3.94	4.5	6.4

*Percentage of commercial pectin in finished jam—11.1; percentage of fruit in finished jam—14.3
†U. S. Food and Drug Inspection Station.
‡This result is entirely too high and must be disregarded.

pulp used in the manufacture of the jam are given for purposes of comparison.

A glance at the table shows very gratifying results for alcohol precipitate. Method I, the tentative A. O. A. C. method, produces high results and should be discarded. This is believed by the referee to be entirely due to contamination with sugar and calcium citrates or malates. Judging from the data obtained by the collaborators, it would appear that Methods II, III and IV are equally reliable. However, it has been the experience of the referee that Method II, in the case of fruits or high pectin jams, does not give as satisfactory results as do the other two methods; it shows slightly high results, probably due to incomplete elimination of impurities. The referee prefers Method III, as it is the simplest.

The pectic acid results are equally good. The referee believes that the pectic acid determination is more reliable than the alcohol precipitate, because it is believed to be a pure compound whereas the alcohol precipitate may not be.

NOTE.—Since the preparation of this report, the referee has had experience in the determination of alcohol precipitate and pectic acid in fruits where water-insoluble substances, of a non-pectic nature, are apt to be more troublesome than in the analysis of jams or jellies. It was found that their precipitation could be generally prevented by adding from 1 to 4 lumps of Domino sucrose to the solutions of fruit during evaporation and about 1 cc. of 10 per cent hydrochloric acid just before the first precipitation with alcohol. If insoluble substances were subsequently encountered, they were filtered off before the final precipitation of the alcohol precipitate or pectic acid. In some cases, especially in the determination of pectic acid in immature fruit, it was found expedient to work with smaller quantities than the directions specify.

The collaborators appear to have found but little difference in the results for water-insoluble solids by the two methods tried. Either one appears to give satisfactory results. This determination should, in the case of jams, give an approximation of the proportion of fruits in the jam.

The collaborators did not agree so well in their sulfur determinations, which was not wholly unexpected. The quantity of barium sulfate weighed is very small and the factor is large. The method for total sulfur is rather tedious and exacting, and it is not surprising that the results do not check closely when first tried by analysts who are not familiar with it. It will be observed, however, that some of the sulfur is lost in the ashing process. The percentage thus lost may vary according to the conditions of the ashing. Determining the sulfur in the ash is by far the simplest method, but not the most accurate.

NOTE.—Since submitting the methods, the referee has determined that quantitative filter papers are not entirely free from sulfur and should, therefore, not be used as a source of organic matter in the blank. Domino sucrose has been found to be sufficiently free from sulfur to serve for this purpose.

RECOMMENDATIONS.

It is recommended—

(1) That a comprehensive study of the composition of the fruits used

in the manufacture of jam and jelly be made to determine the natural variations and to serve as a basis for interpretations.

(2) That further work be done on methods for determining the total sulfur in fruits.

(3) That the present tentative method for alcohol precipitate determination be discarded as unreliable.

REPORT ON THE DETERMINATION OF MOISTURE IN DRIED FRUITS.

By R. W. HILTS (U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, San Francisco, Calif.), *Referee.*

In 1919 this association approved a recommendation that a definite method applicable to the determination of water in dried fruits be formulated and submitted to the association[1]. The present work was undertaken in an endeavor to meet this need, which is a very urgent one among food control officials and manufacturers of dried and dehydrated fruits. At present an official standard limits the moisture content of dried apples and standards for other fruits may be hereafter adopted.

An examination of the present official methods for this determination in dried fruits[2] shows that much latitude both as to method of drying and manipulation is permitted, and the directions are not definite. Briefly, a sample yielding 3 to 4 grams of dried material is to be weighed out, mixed with a few cc. of water, "if necessary to secure a thin layer of the material", and dried to constant weight in vacuo at 70°C. It is not definitely stated whether an absorbent is to be used or not. An alternative method permits drying on quartz sand in a water oven at the temperature of boiling water for 8 to 10 hours with stirring and successive heatings until the weight loss is not greater than 3 milligrams per hour. The accurate estimation of water in foods and especially in those containing much levulose is universally admitted to be a very difficult problem, and anyone with experience in the analysis of dried fruits knows that the latitude permitted will give very discordant results. However, it appears possible that by adopting manipulations especially suited to the product in question and by describing the method very definitely comparable and consistent results reasonably close to the actual truth should be obtained.

Previous work on this subject by the association has resulted in the general conclusion that no method can be recommended which involves heating above 70°C., above which temperature levulose suffers de-

[1] *J. Assoc. Official Agr. Chemists*, 1921, 4: 570.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 101, 153.

composition[1]. Barnard has published results of experiments on dried apples[2], comparing drying at 70°C. in vacuo with that in air and hydrogen at 98°C. at atmospheric pressure. He confirmed the usual observation that the higher temperature caused caramelization and decomposition with continuous loss in weight. The lower temperature in vacuo gave lower and more concordant results but constant weights were not obtained.

The work here described was done by W. T. McGeorge in the San Francisco Station of the Bureau of Chemistry, who also planned it in large part. Many samples of California dried fruits of different degrees of dryness, collected in connection with another investigation, were available. Dried apricots, peaches, pears and apples were used for experiment. Considerable work had previously been done on the determination of moisture in dried apples and raisins. All samples were prepared for analysis by mixing and passing twice through a meat grinder as rapidly as possible and placing in hermetically sealed glass jars. Theoretical considerations as well as much experience having convinced McGeorge and the writer that the method of drying in vacuo at not to exceed 70°C. was the most reliable, the principal effort was directed to a study of this method. A secondary object was to devise, if possible, a simple empirical method not requiring the use of elaborate equipment which would give results close to the vacuum oven and be available for factory control purposes. Experiments were also made with other methods. Drying in an atmosphere of hydrogen at the temperature of boiling water was found to produce as much caramelization as drying in air.

The official method of drying in vacuo over sulfuric acid without heat[3] was also tried, using ether to obtain a high vacuum. After two months' time the samples had only lost about three-quarters of the moisture content indicated by the vacuum oven method and further weighings were discontinued. The distillation method, with the form of apparatus devised by Dean and Stark[4], was given a thorough trial on all four fruits. Xylol, toluol, kerosene, amylacetate and various combinations of these were tried. The results on apples were quite promising but on pears, apricots and peaches results several per cent above the vacuum oven figures could easily be obtained owing to production of water from decomposition. This decomposition appeared to commence long before all the water was expelled, and no point could be selected at which to discontinue distillation. Dried apples in general yield their water rather easily, whereas the other fruits are gummy in texture and dry more slowly.

---

[1] *J. Assoc. Official Agr. Chemists*, 1921, **4**: 54.
[2] *Am. Food J.*, 1915, **10**: 474.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 71.
[4] *J. Ind. Chem.*, 1920, **12**: 486.

The vacuum ovens used were of the cylindrical water-jacketed gas-heated type with shelves of perforated sheet copper. The water jacket was kept nearly full. The temperature of the drying chamber was indicated by a thermometer whose bulb was near the shelves. Three points are worthy of mention: (1) Rarified air is not a good conductor of heat, hence it is desirable that the samples should be placed in metal dishes, resting directly on metal shelves which are in contact with the walls of the oven; (2) a means should be provided for displacing the water vapor by dry air as by admitting through the air inlet tube a slow current of air dried by concentrated sulfuric acid in a gas wash bottle; (3) when a number of moist samples are introduced into a previously regulated vacuum oven, the temperature of the chamber and of the metal shelf promptly drops several degrees and rises again after most of the water is evaporated. If an attempt is made to compensate this cooling effect by application of more heat, it will certainly result in overheating during the latter part of the drying.

The vacuum ranged from 26 to 29 inches of mercury, usually 26 to 28 inches (pressure of 2 to 4 inches), which is as high as can be conveniently maintained by the usual rotary vacuum pump. A considerable number of preliminary experiments were made on the vacuum method at 70°C., using flat aluminum dishes $8\frac{1}{2}$ cm. in diameter with tight fitting covers. The effect of different methods of distributing the sample was tried as follows: (1) Several grams of finely divided asbestos were weighed into the dish with the sample; hot water was added and the whole thoroughly mixed, evaporated on the steam bath just to dryness and placed in the vacuum oven; (2) the sample was smeared over the bottom of the dish with a spatula; (3) the material was simply weighed into the dish without any treatment except to break up any very large lumps. Results using 5- and 10-gram samples were also compared. The differences were negligible or within the limits of experimental error and so a 10-gram sample, without any absorbent or special attempt to spread it, was adopted for further work. It is believed that the larger sample is more likely to be representative simply because dried fruits can not be ground very fine and the mixing of samples is rather difficult.

Next, 3 or 4 samples each of apricots, peaches and pears, prepared as above, were dried in the water oven at the temperature of boiling water (about 98°C.) and in the vacuum oven at 70°C. and weighed at intervals up to about 30 hours. The corresponding drying curves were plotted and studied. Fig. 1 shows these curves for 4 samples of apricots. The others were similar. These curves show very rapid and continuous loss of weight in the water oven, as compared to the lower temperature in vacuo. Experience with numerous samples shows that rate of loss in the water oven also varies with the amount of moisture originally present

and with the variety of fruit in question. This work confirms the general experience that definite results can not be obtained by drying at the temperature of boiling water. The drying curves in vacuo at 70°C. are quite uniform and similar for all the fruits studied. Most of the weight loss occurs in the first 6 or 7 hours. The rate of loss is at first very rapid, then becomes more gradual and after 10 to 12 hours becomes slight and practically constant. However, the rate never becomes zero, i. e. the weight never becomes entirely constant even after long drying.

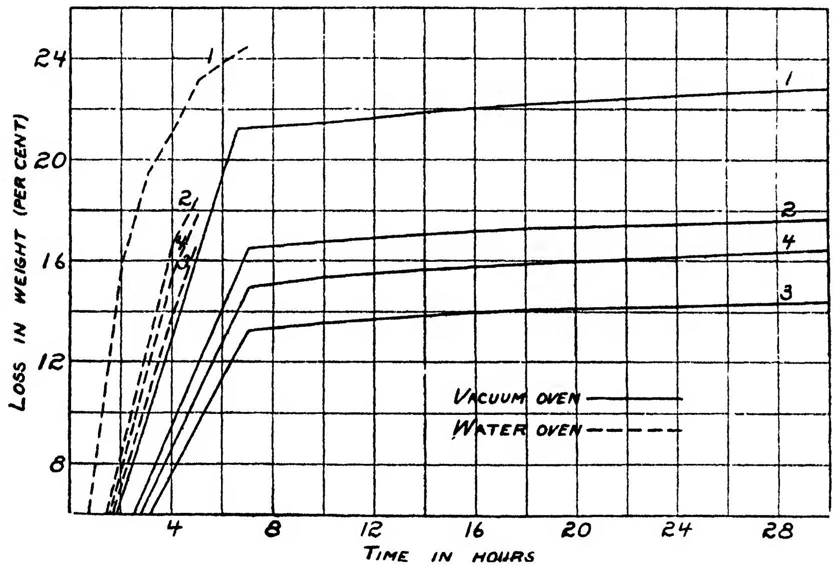


FIG. 1.—FOUR SAMPLES OF APRICOTS DRIED AT 70°C., 26–28 INCHES VACUUM AND IN WATER OVEN, TEMPERATURE OF BOILING WATER

Again, one sample each of apricots, peaches and pears was dried in vacuo at 60°, 70° and 80°C. up to 30 hours. The curves for pears are shown in Fig. 2. All were similar. The rate of loss gradually decreases until, after 10 to 12 hours, it becomes small but constant. The final rate of loss at 80°C. is somewhat greater than at 60 or 70 degrees, indicating the probability of some progressive changes different in kind or in degree from those at lower temperature. This confirms the advisability of not exceeding 70°C. in drying such substances. However, it is quite evident that even at 60 or 70 degrees a slight weight loss will continue almost indefinitely. It can not be said whether this is due to some slow decomposition of levulose or to some other changes. Drying in vacuo at lower temperatures undoubtedly gives results nearer the actual truth than any other method yet suggested, but it is plainly

evident that to get strictly comparable results the temperature, length of drying and degree of vacuum must be more or less arbitrarily fixed. It is self-evident that the bulk of the free water is expelled in the early part of the period; it is highly probable that all of the free water has been removed when the *rate of loss* becomes constant, and that the subsequent loss is due to some form of decomposition. Accordingly, drying a 10-gram sample at 70°C. at a pressure not exceeding 4 inches of mercury for an arbitrary period of 12 hours was adopted as a standard. The method has been used in practically this form in the San Francisco station on thousands of samples of dried fruits, including peaches, apricots, pears, apples and raisins, although the use of 5-gram samples with an absorbent has been found advisable with raisins.

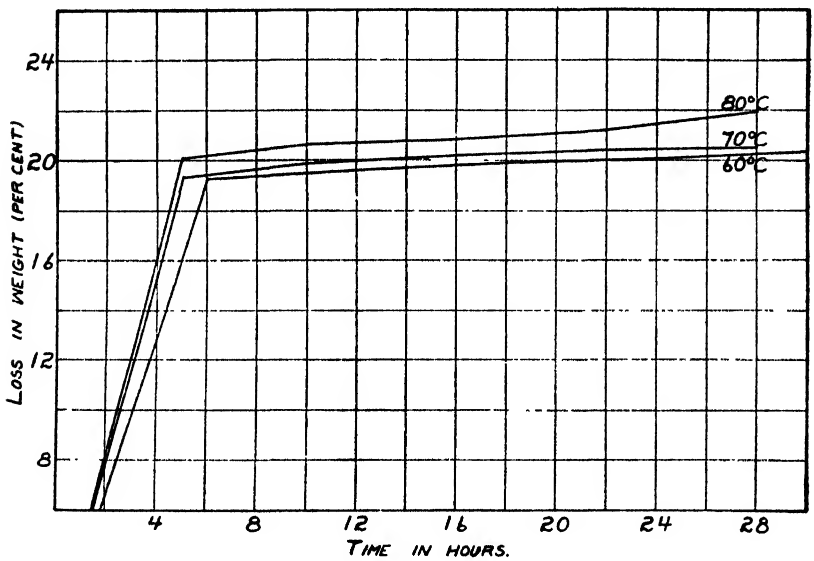


FIG. 2.—SAMPLE OF PEARS DRIED IN VACUUM OF 26–28 INCHES AT DIFFERENT TEMPERATURES.

Past experience with dried apples has shown that drying a 10-gram sample in a metal dish in the water oven at the temperature of boiling water, for a period of 4 hours, gives results quite concordant with the vacuum method above described. An attempt was made to devise a similar rapid empirical method for peaches, apricots and pears. Thirty-seven different samples of apricots, 30 of peaches and 26 of pears were dried by vacuum oven for 12 hours as above, and also in the water oven for three different arbitrary periods selected from a study of the drying curves. These samples ranged from very moist to very dry. The water-oven periods for each fruit giving results which averaged closest

to the vacuum figures were selected for further trial. The results for these optimum drying periods are summarized in Table 1.

TABLE 1.

Determination of moisture at 70°C. in vacuo at temperature of boiling water in water oven.

	APRICOTS (37 Samples)		PEACHES (30 Samples)		PEARS (26 Samples)	
	Vacuum 12 Hours	Water Oven 3½ Hours	Vacuum 12 Hours	Water Oven 4½ Hours	Vacuum 12 Hours	Water Oven 5 Hours
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Average	15.85	15.41	17.90	17.68	24.69	24.77
Maximum difference above vacuum	....	2.00	. .	1.35	....	1.21
Maximum difference below vacuum	..	2.61	. . .	1.50	. .	1.33
Number of results agreeing within 0.5 of vacuum	..	15	....	12	. .	13
Number of results differing by 1.0 or more from vacuum	...	12	.....	6	. . .	4

Composite samples of apricots, peaches and pears in condition as packed were next prepared, allowed to stand in a closed vessel a considerable time to equalize moisture and passed three times through a meat chopper; they were mixed between grindings. Portions were placed in wide-mouth glass-stoppered bottles which were paraffined. Sets of these samples were submitted to every field station and to the Food Control Laboratory of the Bureau of Chemistry. To prevent evaporation collaborators were instructed not to remove the samples from the bottles for mixing, but to mix in the bottle.

The following methods were submitted:

Vacuum Oven Method.

Weigh approximately 10 grams of the thoroughly mixed sample into an aluminum dish 8.5 cm. in diameter, with cover. Dry in a vacuum oven at 70°C. at as high a vacuum as possible for 12 hours. The metal dish must be placed in direct contact with the metal shelf of the vacuum oven without the use of any intervening sheets of paper which might prevent the conduction of heat to the dish. During the drying a slow current of air, dried by bubbling through sulfuric acid, must be admitted to the oven. The rate should be about 2 bubbles per second. At the conclusion of the drying place tops on dishes, cool in a sulfuric acid desiccator and weigh as soon as cool. Report loss in weight as moisture, making duplicate determinations.

If oven is provided with a vacuum gage reading in inches of mercury, as is usual, report the reading of the gage and also the uncorrected barometer reading for the same day. If the oven is provided with a mercury manometer, giving the actual pressure

in the oven, this reading should be reported in place of the above. In your report specify the type of vacuum oven used, whether water-jacketed or electrically heated, etc.

Water Oven Method.

Weigh approximately 10 grams of the thoroughly mixed sample into an 8.5 cm. aluminum dish with cover and dry in a water-jacketed oven at the temperature of boiling water, apricots for a period of 3½ hours, peaches for 4½ hours and pears for 5 hours. After drying for the above periods cool the dishes in a sulfuric acid desiccator as above and weigh. Report loss in weight as moisture, making duplicate determinations. Dishes in the water oven should always be placed on the shelves and not on the bottom of the oven.

If your equipment differed in any manner from the above, describe in detail.

The collaborators' results are given in Table 2.

DISCUSSION.

With one exception the pressures given for the vacuum ovens were obtained by deducting the readings of the vacuum gages from the prevailing uncorrected barometer readings and, on account of the inaccuracy of such gages, are only approximate. With one exception the vacuum ovens were of the water-jacketed gas-heated type. The Seattle station used a Freas electrically heated oven with an inner vacuum chamber. Considering the difficult nature of this determination and the rather elaborate equipment required, it is felt that the results for the vacuum method are quite satisfactory. Very close agreement can not be expected. Of the 92 results reported 68, or 74 per cent, are within 0.5 per cent of the average. It is recommended that this method be submitted another year for study with a view to adoption as official.

The results in the water oven are not satisfactory, due, unquestionably, to differences in size of oven, temperature, ventilation and possibly other factors. The oven temperatures, given by some analysts, varied from 95° to 100°C. The low results of Chernoff are easily explained by the fact that the boiling point of water at the given barometric pressure at Denver would be 94.6°C. and the oven temperature would be a few degrees lower. Hertwig suggested a mechanical device for spreading the sample in a uniform layer, without the use of water, which might give better results. This method is highly empirical, depending on close control of conditions and on the compensation of errors of large magnitude, i. e. the incomplete expulsion of water and decomposition. It is not clear whether it can ever be made reliable for most fruits, and further work is not recommended at this time. However, the case of dried apples is different, since this fruit loses its water with greater ease and uniformity. Experience in the San Francisco station and other Bureau of Chemistry laboratories has shown that drying a 2- to 10-gram minced sample for 4 hours in a water oven gives results quite comparable to the vacuum method. In 1920, at San Francisco, comparative determi-

TABLE 2.

Results of collaborators on moisture determination in dried fruit.

Analyst	Pears		Peaches		Apricots		Average pressure in vacuum oven (Inches of Mercury)
	Vacuum	Water Oven	Vacuum	Water Oven	Vacuum	Water Oven	
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
H. R. Smith, Baltimore, Md.	24.5 24.6	24.5 25.0	23.4 23.5	22.3 23.6	25.2 25.2	25.8 24.0	1.55
C. H. Hickey, Boston, Mass.	24.80 24.83	24.04 23.39	23.42 23.42	21.42 21.03	24.96 24.85	22.92 23.30	0.97
W. C. Taber, Buffalo, N. Y.	*	....	23.1 22.9	23.4	25.2 24.5	26.2 26.4	1.10; occasionally rose to 14.0
L. Jones,† Chicago, Ill.	24.68 24.70	24.56 24.55	23.64 23.62	23.19 22.64	25.47 25.46	24.94 25.29	0.88
M. L. Hitchcock†, Cincinnati, Ohio.	....	....	22.6 22.9	21.8 20.8	24.9 24.9	23.3 22.4	0.14
L. H. Chernoff, Denver, Colo.	24.79 24.69	21.63 19.29	23.57 23.58	17.88 20.85	25.52 25.26	20.71 21.82	0.10
D. B. Scott, Washington, D. C.	24.34 24.21	24.07 23.66	23.21 23.32	22.66 22.77	25.30 25.28	25.07 25.17	3.0 to 5.0
J. I. Palmore, Washington, D. C.	24.42 24.51	24.81 25.09	23.21 23.19	23.72 24.09	25.29 25.09	25.01 25.57	1.50
L. C. Mitchell, Minneapolis, Minn.	25.2 24.9	25.7 26.4	23.0 21.9	23.5 24.2	24.3 24.9	25.7 25.8	0.32
F. L. Elliott, New Orleans, La.	23.47 23.43	24.29 24.50	22.23 22.15	21.24 21.35	23.94 24.05	24.29 24.88	6.0
M. Ruderman, New York, N. Y.	23.93 24.07	24.33 23.51	22.83 22.73	21.38 22.31	24.56 24.45	23.71 23.13	3.5
C. S. Brinton, Philadelphia, Pa.	24.50 24.47	22.08 21.17	23.05 22.97	20.83 19.06	24.82 24.79	21.14 22.37	0.23 to 0.39 (manometer)
R. Hertwig, San Francisco, Calif.	24.37 24.59	23.54 24.28	22.70 22.73	22.78 23.05	24.18 24.27	23.42 24.42	1.29
J. Calloway, Jr., Savannah, Ga.	24.73 24.76	24.49 24.57	22.87 22.94	23.05 23.34	24.96 24.99	24.61 24.73	0.92
V. B. Bonney,	24.32	24.97	22.70	23.12	24.13	24.56 25.42	0.10
D. H. McIntire, Seattle, Wash.	24.25	24.88	22.68	22.90	24.41	25.46 24.48	0.10
D. B. Bisbee‡ St. Louis, Mo.	24.85 24.68	24.70 24.98	23.74 23.65	23.95 23.54	25.65 25.64	26.23 25.49	3.41
Maximum	25.2	26.4	23.74	24.2	25.65	26.4	
Minimum§	23.43	21.17	21.9	19.06	23.94	21.14	
Average§	24.49	24.31	23.04	22.52	24.89	24.54	

*Sample arrived in bad condition.
†Used double-wall steam-heated ovens instead of water ovens.
‡Used a ventilated electric oven, temperature 98° to 100° C., instead of water oven.
§Excluding results of Chernoff in water oven. See discussion.

nations were made by both methods on 52 different samples, using 10 grams. The average for the vacuum oven was 23.59 per cent and for the water oven 23.69 per cent. In only seven of these samples was the difference between the methods greater than 0.5 per cent, and it was usually very much less. It is believed that this method should receive further attention with a view to adoption as a tentative method, on account of its great practical value.

It is suggested that future work should include an attempt to determine moisture by some method depending on a totally different principle, as the calcium carbide method described by McNeil[1].

RECOMMENDATIONS.

It is recommended—

(1) That the following method for the determination of moisture in dried fruits by drying in vacuo be studied for another year with a view to adoption as official:

Weigh about 10 grams of sample into a metal dish about 8.5 cm. in diameter, provided with a cover, breaking down any large lumps. Dry in vacuo at 70°C. for 12 hours at as low a pressure as possible, not to exceed 4 in. (100 mm.) of mercury. During the drying admit to the oven a slow current of air, about 2 bubbles per second, dried by bubbling through concentrated sulfuric acid. The metal dish must be placed in direct contact with the metal shelf of the oven. Replace cover, cool in a desiccator and weigh. Disregard any temporary drop of oven temperature which may occur during the early part of the drying period owing to rapid evaporation of water.

(2) That the following method for the determination of moisture in dried apples be further studied with a view to adoption as tentative:

Weigh 5 to 10 grams of sample into a metal dish about 8.5 cm. in diameter, provided with a cover, breaking down any large lumps, and dry for 4 hours in a water oven at the temperature of boiling water. Replace cover, cool in a desiccator and weigh. Place dishes on shelves and not on oven bottom. Temperature of the oven should not be below 96°C.

(3) That an attempt be made to determine moisture in dried fruits by some method depending on a totally different principle, as the calcium carbide method.

---

[1] U. S. Bur. Chem. Circ. 97: (1912).

REPORT ON CANNED FOODS.

By R. W. Balcom (Bureau of Chemistry, Washington, D. C.), *Referee.*

The referee regrets that, owing to his appointment by the Executive Committee to fill the positions of secretary of the association and chairman of its Board of Editors, made vacant when Dr. Alsberg severed his official connection with the United States Department of Agriculture and therefore with the association, he found little time to give to the work on canned foods. The association had recommended that the investigation of methods for the detection of spoilage and for distinguishing conditions which are likely to lead to spoilage be continued.

R. S. Breed and C. A. Darling of the New York Agricultural Experiment Station, Geneva, N. Y., submitted some recommendations for changes in the wording of the Howard methods[1] for the micro-analysis of tomato pulp, catsup, purée, sauce and paste. The suggested changes are for the purpose of securing greater clearness or accuracy of statement. They are as follows:

It is recommended that under XIII, 28, the third paragraph be changed to read—

Place the slide under the microscope and examine with a magnification of about 90 diameters and with such adjustment that each field of view covers[2] 1.5. sq. mm. This area is of vital importance and may be determined by adjusting the draw-tube in such a way that the diameter of the field becomes 1.382 mm. as determined by measurement with a stage micrometer. A 16 mm. Zeiss apochromatic objective with a Zeiss X6 compensating ocular or a Spencer 16 mm. apochromatic objective with a Spencer X10 compensating ocular, or their equivalents, shall be used to obtain this magnification. Under these conditions the amount of liquid examined is 0.15 cmm. (0.00015 cc.) per field.

It is recommended that in XIII, 29, line 4 of the third paragraph "1/60 cmm." be changed to read "1/60,000 cc."

It is recommended that XIII, 30, be changed to read—

BACTERIA.—TENTATIVE

Estimate the number of rod-shaped bacteria from the mounted sample used in 29 but, before examination, allow the sample to stand not less than 15 minutes after mounting[3]. Employ a magnification of about 500, which may be obtained by the use of an 8 mm. Zeiss apochromatic objective with an X18 Zeiss compensating ocular with draw-tube not extended, or an 8 mm. Spencer apochromatic objective with an X20 Spencer compensating ocular and a tube length of 190, or their equivalents.

Count and record the number of bacteria having a length greater than 1½ times their width in an[4] area consisting of five of the small sized squares. Count five such areas, preferably one from near each corner of the ruled portion of the slide and one from near

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 164.
[2] Matter deleted.
[3] Matter deleted.
[4] Matter deleted.

the center. Determine the total number of the rod-shaped bacteria in the 5 areas and multiply by 480,000. This gives the number of this type of bacteria per cc. If a dilution of 1 part of the sample with 8 parts of water, instead of 1 part of the sample with 2 parts of water is used in making up the sample, then the total count obtained as above must be multiplied by 1,440,000. Thus far it has proved impracticable to count the micrococci present as they are likely to be confused with other bodies frequently present in such products.

These recommendations are approved by the referee and the author of the methods with the exception of that in which it is suggested that "1/60 cmm." be changed to read "1/60,000 cc."

RECOMMENDATIONS.

It is recommended—

(1) That the changes in wording of Howard's methods for the micro-analysis of tomato pulp, catsup, purée, sauce and paste, proposed by Breed and Darling of the New York Agricultural Experiment Station, Geneva, N. Y., be adopted, except for the proposed change by which "1/60 cmm." in XIII, 29, paragraph 3, line 4 would be made to read "1/60,000 cc." It is not believed that this change is advisable. Practically the same end can be attained without changing the unit 1/60 cmm., heretofore used, by inserting immediately following it, in parentheses, the equivalent expression 1/60,000 cc., and it is recommended that this be done.

(2) That the methods for the micro-analysis of tomato pulp, catsup, purée, sauce and paste, with the changes in expression specified, be adopted as official.

A NET MICROMETER FOR USE IN MAKING MOLD COUNTS.

By B. J. Howard (Bureau of Chemistry, Washington, D. C.).

In the tentative official methods for the microscopic examination of tomato products the analyst is directed that "no field should be considered positive unless the aggregate length of the filaments present exceeds approximately one-sixth of the diameter of the field". With the apparatus as usually employed the determination of this length of filament becomes merely a question of individual estimate and judgment since there is no scale in the field of view to use for comparative measurements.

Some time ago C. H. Stephenson and W. K. Makemson of the Microchemical Laboratory of the Bureau of Chemistry suggested having the mold-counting chamber ruled in squares of 0.23 mm. on a side (1–6 of 1.382 mm. the diameter of the field of view). A chamber of this con-

struction was obtained and tested out, but it was found that some tomato products were of such consistency as to render invisible part of the fine rulings, thus limiting its practicability. Later Stephenson suggested a drop-in eyepiece micrometer ruled in squares equal to one-sixth of the diameter of the opening in the eyepiece diaphragm. Inasmuch as the size of the opening varies in different makes of eyepieces the disk must be ruled accordingly, after a careful measurement of the diameter of opening has been made. Such a micrometer was given a preliminary practical test by two members of the Microchemical Laboratory, and they report enthusiastically in its favor. It has two definite advantages over the ruled chamber as first proposed, namely, (1) that the rulings are always in plain view and (2) the ocular with the disk can be instantly rotated to effect parallelism with the mold filaments being measured.

From the practical tests which have thus far been made with it, it is believed that the introduction of this device will help eliminate the personal factor of judging the length of filaments by those using this mold-counting method. Fortunately its employment does not introduce any change whatever in the method itself.

ADDRESS BY THE HONORARY PRESIDENT.

H. W. Wiley (Good Housekeeping, Bureau of Foods, Sanitation and Health, Washington, D. C.).

It is with very great pleasure that I am able to be here today. Without ever consulting me you changed the time of your meeting and came very near depriving me of the great pleasure which you have just been told you have. If I had not had a good deal of influence with my surgeon I would not be here today, but when I told him that the interests of the country were involved and that I must have leave of absence for this meeting, he very reluctantly allowed me to come. I can hardly say that I take pleasure in seeing you because my seeing days are temporarily in eclipse, but I hope with the aid of the skilful surgeon's knife to be able really to see you at this time next year.

I was much interested in and instructed by the two papers to which I was privileged to listen this morning. In the first paper the importance of expressing all business relations in chemicals in metric units was stressed. I wonder if you realize how important that question is today. For 25 years or more, yes, since 1866, efforts have been made to introduce a simple system of measurements into this country. In 1866 the only system of weights and measures ever legalized by Congress was adopted, the metric system, so called. Our Constitution authorized

the Congress of the United States to coin money and to regulate or establish standard weights and measures. Our fathers understood the importance of this matter and so incorporated it into the first section of the Constitution. They also ordained and established a decimal system of money, and I doubt if the most rabid opponent of the metric system in business in this country would dare advocate going back to the old system of pounds, shillings and pence. So Congress, in 1866, legalized the metric system. I do not suppose Congress would do it now—there would be such an opposition to it—but in those days nobody had ever heard of the metric system and therefore there was no opposition. If you want to get really good legislation, slip it in. That was the way I got into the appropriation bill the authority to inspect imported food products four years before the National Food and Drugs Act was inaugurated. Nobody ever noticed it, and it went through for that reason. They began to notice it thereafter, but not in time.

In 1873, in my first paper read before the American Association for the advancement of Science, entitled "The Introduction of the Metric System into Medicine", I pointed out the advantages which would accrue to the medical profession and the pharmaceutical profession by the adoption of that simple system of weights and measures. That bore fruit earlier than I had anticipated, because in 1894 the Congress of the United States passed a law requiring the use of the metric system of weights and measures in all the medical departments of the United States Government. The Pharmacopœia of the United States in the 9th revised edition has incorporated the metric system as the sole system legalized by the Pharmacopœia, but it gives in parentheses the ordinary system for the convenience of those who have not had time to forget the old. I won't say have not had time to learn the new one because it takes no time, but those who are incapable of forgetting have to have a little sop thrown to them in the Pharmacopœia, 9th Revised Edition. There is now before Congress the annual bill to establish the metric system of weights and measures as the sole system to be used in this country, and the usual opposition, of course, is manifested. We are told that it will disarrange business, scrap thousands of dollars' worth of models, impose untold hardships on the American manufacturer, obfuscate the farmer and all such gaff, which we are accustomed to hear in the case of all really great reforms. When I was before the committee the other day the chairman of the subcommittee to consider this matter made this objection. He said: "I would not mind these objections of the business men but the farmers would be hard hit if they had this system imposed upon them". And I promised to bring facts before him to show him how the farmers will be the parties that are chiefly benefited by this system of weights and measures; how the farmer buys a short ton and sells a long ton and is defrauded out of

about 200 pounds by the operation; and how the farmer in one State, if he sells a barrel of products in another State, runs into a different form of valuation. The Bureau of Standards has published a list of laws, State laws—not municipal but just State laws—showing the innumerable systems of weights and measures in use in this country. The publication is a small volume, in fine print, of 694 pages. If it attempted to give the laws of the municipalities, another volume equally as large would be required.

Now, if we want relief from a great and intolerable burden, we want that suggestion made by the speaker this morning adopted, not only for drugs and chemicals but for everything that we buy and sell. Why should we delay any longer lifting this burden from the shoulders of our children? They begin in the first grade to try to learn weights and measures; they continue through all the eight grades, the high school, the college, and all through life, and then never learn anything of value. I do not suppose there are four persons in this audience who can tell the value of a fathom or a furlong. I found my older boy had learned three things in four years, and one of them was wrong. I said: "How many ounces in a pound"? Immediately he responded twelve. That boy is going to be a pharmacist, I am sure. His pound was the troy pound. And then I said: "What is the metric system, my son"? He said: "The metric system is something that falls out of the sky". He thought it was the meteoric system I was asking about. Now he did know that there were twelve inches in a foot and three feet in a yard. Those were the only things he had learned in four years of effort, and he is still trying every day to learn something more.

Another thing struck me this morning in that wonderful address of the President. I am almost convinced that chlorophyl is about as important as the *Saccharomyces cerevisiae*. You see the sop that was thrown to the brewers this morning by the ruling of the Secretary of the Treasury that the homeopathic doctor prescribing for his patient any homeopathic dose may write a prescription of two gallons and a half! Now that is going some for a homeopath, isn't it? So you see the little bug is not dead yet. But now this chlorophyl is going to run the race also to become commercialized just as soon as this paper of the President gets into the public press and people begin to talk about it. You will have chlorophyl cakes to cure pimples; and you will have chlorophyl tooth paste to cure pyorrhea; and you will have chlorophyl beauty soap for the young ladies; and it will run the whole gamut that yeast has run in the last few years. I do not know but that we ought to hale Atherton Sidell before this organization and try him for treason because he with the aid of John Uri Lloyd was able to isolate and separate vitamines from yeast. Look at the yeast propaganda that is going on all over the world! Knowing that I was to make an

extemporaneous address I brought some of this with me, just to show you how it is going and what rate of speed it is making. Here it is: "Vitamines extracted from yeast, combined with fat, soluble vitamines etc. into a proper dose; tablets easy to take; results guaranteed; cure all the diseases to which the human flesh is heir". And here again is "Yeast beauty soap, containing pure yeast, price 25 cents, for skin and scalp"; "Yeasto tooth paste"; "Yeasto beauty soap". So you see what your friend, chlorophyl, is coming to. This yeast campaign has in fact broken into the realms of poetry, as one poet has written:

Fresh milk and greens give vitamines
Enough for little Sid,
So he at least will need no yeast,
A real self-rising kid.

I suppose that it would not be out of place if I should just run over a few of the things in the realm of chemistry and agricultural chemistry which have occupied the public mind since we last met. I think the outstanding feature was the visit to this country of Madam Curie. Never was a scientific man or woman accorded such honors as were given to her. She was received by the President of the United States in the historic East Room as the Prince of Wales or Lloyd George would be received and with equal honors, and she was met there by a company of people especially invited to meet her, representing the very best of American scientific and social life. There this modest little woman who would not attract attention, except perhaps by someone offering to help her across the street—she seemed so timid and unpretentious—was the recipient of honors which are paid only to royalty and to rulers. In addition to that, the heartfelt sympathy and gratitude of the great American people were expressed by a gift which in pecuniary value probably is larger than any ever presented to a visiting potentate or ruler of the world.

This features the progress that chemistry has made in the minds and hearts of our people. Who could have imagined forty or fifty years ago that such honors would be paid to a chemist? And the more we know—or the less our ignorance is perhaps would be better—of radium, the more wonderful do the achievements of this woman appear. We sometimes wonder whether she or her husband was the real discoverer. I am certain it was Madam Curie because radium is so like a woman that I do not believe any man could ever have discovered it. Its peculiarities, its reactions and inter-reactions, its violation of all the rules of ethics and of scientific accuracy, its snapping of fingers at gravity, the rules of combination and the integrity of matter all stamp it as feminine. All the other elements may be masculine or neuter, but radium is distinctly feminine, and I propose that we call it radia

because that is the feminine form that it ought to bear, instead of radium, which is neuter.

After I found I was to come to this meeting I attempted to summarize the real benefits received and the progress which had been made in agriculture as the result of the formation of this association. Now it seems to me that we measure these largely from the scientific and not from the economic point of view. I mean that the benefit from this association to agricultural chemistry is largely scientific—bringing together the workers into a harmonious organization of great solidarity and persistence and working a great influence on the scientific world, thus adding to science that unity of purpose, of design and of effort which is necessary to effect great changes and get great results. But when I come to look at the crop reports and compare them with those of thirty or forty years ago, when this association was first formed, I fail to see that our work has been reflected in any way in increased production. The yields of our crops are due largely to seasonal influences. In other words, the variety of yields is not due to any systematic application of the principles of scientific agriculture which this association has inculcated. If you go out among the farmers you will find that while they use commercial fertilizers much more extensively than they did in the old days, as a rule the actual yield of crops has not been very greatly increased. Our wheat still stands around about 13 bushels per acre in a series of ten years, and our yields of Indian corn about 27 bushels per acre in the same length of time. Now that condition, of course, will not continue. There must soon be a reflection of the activities of the association in an economic sense because we need larger yields. Our tillable areas are now largely occupied. When we recover from swamps or from deserts an additional acre, it is at an investment which places its initial value very high, so that a cheap crop can not profitably be grown upon it. In this association we must all insist, for economic reasons, upon a better yield or a better system of crop rotation and crop selection. In other words, if it costs a hundred dollars to reclaim an acre of land one can not afford to grow 13 bushels of wheat upon that acre, or 27 bushels of Indian corn. It does not pay because of the initial investment. Hence, in the reclaimed areas scientific agriculture is necessary; but in the old areas of broad and wide agriculture it is not yet a necessity. We see the crops of wheat diminishing, the yield per acre falling, and we do not have those wonderful yields that we had a few years ago. It is true that on the Pacific coast there are still some phenomenal yields. At this time last year I was on the Pacific coast and attended a fair in the State of Oregon. I saw wheat placed there on exhibit by the State Board of Agriculture, with a yield of 115 bushels per acre! It was not very good wheat; it was soft and would not make high-grade flour, I imagine,

but it was there and showed the capacities and possibilities of agriculture in that region. But we have no such yields here. We can get a yield of 100 bushels of corn to the acre here—it has been repeatedly done in nearby places—and of thirty or perhaps forty bushels of wheat, although I have never seen a field that measured forty.

The relation of yield per acre to population is a great question you know, and it is not reflected in a corresponding increase in the number of persons engaged in agriculture. There are more people to be fed and the agriculturists are hardly able to do it, without being forced into a systematic, scientific agriculture which will greatly increase the yields of crops. This I expect to see accomplished in the near future as one of the results of the organization of this association.

Another feature that I want to speak of is the progress that has been made in the utilization of foods for dietary purposes. The human animal has really waked up to the fact that he is quite as important from the dietary point of view as the pig or the cow or the sheep. For years we have known all about the scientific feeding of domesticated animals, and now we are about to learn something about domesticated babies and how they should be fed. Our systems of diet are just on the point of change, and they will change very rapidly. I attended, last week, that wonderful health exhibit at Cincinnati, one of the first of the kind in this country. Another, similar to the one in Cincinnati and probably on a larger scale but not on a better scale, will be held in New York about the middle of November. I saw the University of Cincinnati exhibit of dietary substances, and it was wonderfully informing and interesting. One of the peculiarities of human nature is that side by side with that was an exhibit of the Coca Cola Company. There I found the health exhibits of the Health Office and of the Public Schools and learned what a child should eat at its noon-day meal and everything of that kind, reflecting all the modern progress that has been made in the last ten or fifteen years on dietary studies. I saw there in operation a mill cleaning and grinding whole wheat flour. I saw exhibits of cereals that contained all the vitamines that little Sid needs without eating yeast; the featuring of leaf vegetables and undegerminated and undecorticated and undenatured cereal products. The people of this country are realizing the danger that comes from the eating of refined foods. Now, I have always been an advocate of pure foods, as you know, and I find I have always been wrong because pure foods will not nourish. This has been demonstrated time and time again. If you feed pure fat, pure protein, pure carbohydrates, pure minerals, the animals will starve to death. So, after all, the impure foods are necessary to health and vitality, not the kind of impurities that have been visited upon us, but natural foods as Nature put them up. Nature certainly knows her job when she decrees that the diet

shall be colorful. We do not appreciate color as we should. We should all be artists because the chrome is a great thing not only in vegetation, but in animal life. The very beginnings of animal life are the colorable products, chromosomes, just as wonderful as the chlorophyl, the xanthophyl and the erythrophyl, which condition heredity. What would the October days be without the change of chlorophyl into xanthophyl and erythrophyl? The artist will paint the forest and the woods and gratify the eye and the aesthetic taste of the people who look at them. We do not appreciate as we should the value of color, not only in art and beauty but in vitality and health. I am not surprised to find that the vital principle of vegetable growth, the vitamine, is a color lover because vegetable growth is distinguished by color just as the chromosomes are the vital principles of animal life. The blood of life of the animal is a color substance. It is the colorless substance that is free of vitamines; they are always associated with color. So life is indelibly associated in every respect with color, both at its inception and through its whole progress. I think this progress in dietary chemistry is the outstanding mark in chemistry in this country during the past three or four years and will continue to be until we find out more definitely what these vitamines are and how they perform their function. We do not know their chemical composition; we do know they resemble in some respects the catalases. They induce reaction even if they do not take part in it, and hence nutrition without this element is impossible. And thus the argument for natural foods becomes imperative and will make its impression even upon the doctors of this country in the course of time. I hope to live until I see doctors who will prescribe a food for an infant with some rhyme and reason, instead of empirically using sweetened condensed milk because it is easy to prescribe and because the child when it dies looks fat and healthy, and that is a great comfort to the mother.

If our work as chemists and scientific men reflects itself in this way in public service, then we will not be unrewarded. I wonder sometimes why it is that while in foreign countries scientific men take a great part in governmental affairs and have always done so, our scientific men do not become more active. They do not consider it beneath their dignity to give public service, and especially when they have made their career and have acquired a competence. I can understand why a scientific man in the early part of his career does not like to abandon it and give himself to politics; it is because there is nothing in politics to reward him, except service, and he can get plenty of that and get mightly little reward from a monetary standpoint. But when a scientific man does acquire a competence and does have time to give himself to public life, why doesn't he? We have had two chemists at least in the House of Representatives, and now we have one chemist in the

Senate. I understand he is not here today; he is probably detained for some political reason rather than some scientific reason. But the fact that he, our own colleague, is in the Senate is a great consolation to all of us.

It is plain that the scientific man has to serve humanity not only in his profession, but in every possible way for we are all human beings. As we all belong to the great commonwealth we should not be selfish in our activities. So I hope that in the future more scientific men will be able to enter the halls of legislation and give themselves largely to the public service. That I would consider one of the great marks of progress.

We have almost perfected the systems of animal feeding. We know exactly what foods to use for the kind of service we need, and we find the same system good for the human animal We should not feed every human animal alike. If a boy is going to be a prize-fighter, of course he should largely have punch in his food, but if he is going to be a minister of the gospel he should be fed on angel's food, although that has no vitamines in it, I am sorry to say; but still that would be the logical thing to do. In other words, if a man leads an active physical life his food should be different from that of a man in sedentary employment. There is no question about that. And the foods in the summer should be different from those in the winter and less in quantity because less heat is required in summer. All these things have been neglected up to the present time, but now through health exhibits as in Cincinnati and in New York next week, and through the public press the good work goes on. The newspapers featured this exhibit in Cincinnati as they would the series for the baseball championship, making it the real outstanding feature of the week. So, I say, we should devote ourselves first of all to our scientific studies and to the solution of such problems as your President has elucidated in such a charming way. That is our first duty. Then we have another duty—to serve the people of this country in every possible way and with every possible power and effort which we can command.

W. F. Hand.—Dr. Wiley has placed us under renewed obligations. Nothing I can say in your behalf would give him any assurance of our increased appreciation. We can only indulge a hope that we will meet here next year and year after year for many years to come and assure him of our love and esteem.

Dr. Wiley referred to Dr. Ladd's absence. He expected to be here and he wants the association to know that it was only through the direst necessity that he was compelled to be away.

B. B. Ross.—Reference has been made to the fact that one of our most distinguished members, a former president of this organization,

has now been called into the service of his country. He is a member of the highest branch of our national legislative body, and I feel sure that he was called to that position by reason of the service that he rendered to the people of his State in the cause of pure food and improved methods in agriculture. In recognition of his long service in the field of agricultural chemistry and in the cause of pure food, I move that although his active official connection with this organization has been severed, he be elected an honorary life member of the Association of Official Agricultural Chemists. I refer to Senator E. F. Ladd.

William Frear.—I desire to have the honor of seconding this motion.

The motion was carried unanimously.

SECOND DAY.

TUESDAY—AFTERNOON SESSION.

REPORT ON CEREAL FOODS.

By C. H. Bailey (Agricultural Experiment Station, St. Paul, Minn.), *Referee.*

The Committee on Referees, at the 1920 meeting, recommended that the work on the determination of moisture, gluten, soluble carbohydrates, cold water extract, chlorine and ash be continued; and that the referee study methods for the determination of fat in baked cereal products.

Since it is impossible to carry work on all these methods simultaneously with the limited number of collaborators interested in cereal foods, the referee and the associate referee selected what appeared to be the methods most urgently needing development. These were (1) methods for the determination of fat in baked cereal products, the results of collaborative studies being included in this report; and (2) the quantitative determination of chlorine in bleached and natural flours, which is reported by the associate referee.

While a number of methods for the determination of fats in baked cereal products based upon the Polenske method[1] have been discussed in the literature, two methods developed in the Bureau of Chemistry seemed worthy of collaborative study. The first, for the determination of fat in alimentary pastes, noodles, etc., was suggested by R. Hertwig; the second, by C. R. Smith, was for essentially the same products. With the advice and assistance of the associate referee, the following instructions were prepared and distributed to the several collaborators, together with two ground samples of bread (A) and ordinary soda biscuit or "crackers" (B):

The collaborators will determine in duplicate the fat content of Samples A and B by each of the two following methods:

Method I.

Place 2 grams of the finely divided material in a 50 cc. beaker. Add 10 cc. of hydrochloric acid, sp. gr. 1.125. Heat the beaker and contents in a water bath maintained at 65°C. until particles are broken up, and everything except fibrous material is in solution. During this heating (10–15 minutes) stir the material in the beaker with a glass rod in such a way that the rod touches the sides of the beaker from top to bottom. Cool; then add 10 cc. of 95% alcohol. Finally cool in a bath of melting ice and pour

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 249.

the "solution" into a Mojonnier extractor[1], washing the beaker with several portions of ethyl ether, 25 cc. in all being used for this purpose. To the mixture in the Mojonnier extractor, add 25 cc. of petroleum ether (boiling point below 60°C.). After mixing, allow to settle, and carefully decant off the ether layer into a weighed flask or "fat bulb". Add 50 cc. of a mixture of equal parts of ethyl and petroleum ether to the material remaining in the Mojonnier extractor, and again decant into the same flask. If the ether layer has been thoroughly drained from the aqueous layer each time the two treatments with mixed ethers will suffice; if incomplete drainage is effected a third extraction should be made with the mixed ethers. The ether in the combined extracts is distilled off over a steam bath; the flask and contents are dried at 100°C. for 30 minutes, cooled, and weighed from a desiccator.

Method II.

Place 5 grams of ground sample in a 200 cc. Erlenmeyer flask and add a mixture of 10 cc. of 95% ethyl alcohol, 2 cc. of concentrated ammonia and 3 cc. of water. Cap with a short-stemmed funnel, tip downwards. Maintain contents of the flask at the boiling point over a steam bath for 2 minutes. Cool and extract the mixture with 3 successive portions of ethyl ether of 25 cc. each, kneading and tamping the matted material *thoroughly* each time with a glass rod flattened at the end. Combine the ether extracts in a 200 cc. flask. The last portion of ether must be drained off as completely as possible or it will later cause trouble[2]. To the solid residue in the flask, add another 15 cc. portion of the ammoniacal alcohol mixture and repeat the entire operation, except that the period of boiling on the steam bath should be extended to 15 or 20 minutes in order to disintegrate the glutinous mat of solid material. Then distil off the ether in the combined extracts, heat the latter to dryness on the steam bath, cool, and extract the fatty residue in the flask with several successive portions of a mixture of equal parts of ethyl and petroleum ether, using about 25 cc. in all for this purpose. Collect these extracts in a tared beaker or "fat bulb", evaporate to dryness on a steam bath, dry in an oven at 100°C. for 30 minutes, cool and weigh.

The reports of collaborators are summarized in Table 1.

DISCUSSION.

From the comments accompanying the reports, it is evident that the phraseology of the methods should be changed in one particular, and that is to dry the fatty residue in the bulb or flask to constant weight, since 30 minutes was not necessarily sufficient to volatilize all the mixed ethers used as fat solvent.

With the Smith (II) method the results are quite satisfactory, particularly with the sample of crackers (B). The variation in results with the sample of bread (A) may possibly be attributed to the lack of homogeneity in the sample, consisting as it did of a mixture of dried crust and crumb fragments. It was suggested that a finer subdivision of the material might have contributed to greater uniformity in the analytical findings. Hertwig's method (I) resulted in much wider

[1] NOTE.—Mojonnier extractors can perhaps be made by constricting a large-bore (1¼ inch diameter) test tube about 1 inch from the bottom and a like distance from the top, and bending slightly at the constrictions to the angles shown in the cuts of this device.

[2] NOTE.—Failure to drain out the ether completely at this point necessitates a cautious and gradual heating with the second portion of ammoniacal alcohol solution, as the ether must be distilled off before the mixture can be brought to the desired boil. Otherwise disastrous bumping will occur, and part of the solution may be thrown out of the flask.

variations in the results, particularly with the ground crackers (B), and even when employed by the same analyst, as shown by the report of Rask.

TABLE 1.

Results of collaborative study of two methods for the determination of fat in baked products.

ANALYST	METHOD I		METHOD II	
	Bread (A)	Crackers (B)	Bread (A)	Crackers (B)
	per cent	*per cent*	*per cent*	*per cent*
C. B. Morison, American Institute of Baking, Chicago, Ill.	..	...	2.25	10.43
	....	..	2.58	10.50
J. L. St. John, Agricultural Experiment Station, Pullman, Wash.	...	...	2.62	10.61
	....	....	2.63	10.64
C. M. Fritz, Howard Wheat and Flour Testing Laboratory, Minneapolis, Minn.	2.15	4.65	3.57	10.38
G. S. Taylor, Agricultural Experiment Station, St. Paul, Minn.	2.78	9.68	2.92	10.67
	2.72	9.88	2.95	10.50
C. E. Goodrich, Bureau of Chemistry, Washington, D. C.	1.83	6.97	2.52	10.70
	1.87	6.54	3.40	10.76
	....	6.51	2.90	10.73
Ruth Buchanan, Bureau of Chemistry, Washington, D. C.	....	..	3.20	10.72
	..	..	3.13	10.78
O. S. Rask*, Bureau of Chemistry, Washington, D. C.	1.96	8.94	2.92	10.62
	2.08	9.96	2.89	10.75
	2.19	7.35	...	...
	.	8.32	..	.

*Present address, University of Minnesota, University Farm, St. Paul, Minn

The referee concluded that the present official ash and moisture methods are so adequate as hardly to justify further collaborative study at this time. The principal difficulty now is to insure that cereal chemists actually employ the official methods, since it is evident that many of them are following other methods. The referee also believes that the determination of cold water extract is not of sufficient value to justify collaborative study until further research develops the changes occurring during the process of extraction and the character and significance of the solids in the extract.

RECOMMENDATIONS.

It is recommended—

(1) That collaborative work on the determination of cold water extract be discontinued.

(2) That work on the determination of moisture and ash be discontinued until further research develops more desirable methods.

(3) That the following method for the determination of fats in baked cereal products be adopted as a tentative method and be subjected to further collaborative study:

Place 5 grams of ground sample in a 200 cc. Erlenmeyer flask and add a mixture of 10 cc. of 95% ethyl alcohol, 2 cc. of concentrated ammonia and 3 cc. of water. Maintain contents of the flask at the boiling point over a steam bath for 2 minutes. Cool, and extract the mixture with 3 successive portions of ethyl ether of 25 cc. each, kneading and tamping the matted material thoroughly each time with a glass rod flattened at the end. Pour off the ether layer by decantation into a 250 cc. beaker. The last 25 cc. portion of ether should be drained off as completely as possible. Add another 15 cc. portion of the ammoniacal alcohol solution to the extracted residue in the flask and disintegrate the matted material as thoroughly as possible by means of the flattened glass rod which should be left in the flask for this purpose. Return the flask to the steam bath and repeat the entire procedure, prolonging somewhat the treatment with ammoniacal alcohol. Add the ether extracts to those obtained before. Evaporate the combined extracts to dryness on the steam bath, and then extract the fatty residue with 5 or 6 successive portions (about 15 cc. each) of a mixture of equal volumes of ethyl ether and petroleum ether. Collect the extracts in a tared dish (do not try to filter) and evaporate to dryness on a steam bath. Dry the residue to constant weight in an oven at the temperature of boiling water, cool in a desiccator and weigh.

STUDIES ON WHEAT FLOUR GRADES, III—EFFECT OF CHLORINE BLEACHING UPON THE ELECTROLYTIC RESISTANCE AND HYDROGEN ION CONCENTRATION OF WATER EXTRACTS[1].

By C. H. Bailey and Arnold Johnson (Division of Agricultural Biochemistry, Minnesota Agricultural Experiment Station, St. Paul, Minn.).

Bleaching of flour with nitrogen peroxide can be detected more readily than similar treatment with chlorine. Through the use of the Griess-Ilosvay reagent[2] the test for nitrogen peroxide can be made either qualitatively or quantitatively. A qualitative test for chlorine bleaching has been suggested by Alway and Gortner[3], in which the fat from suspected flour is ignited in a flame on a freshly oxidized copper wire. On page 1512 they say: "If chlorine or bromine has been used as a bleaching agent a green or blue coloration is produced". Chlorine can be determined quantitatively in the flour, and Utt[4] found appreciable differences in the total chlorine content of bleached and unbleached flours. Jacobs[5] devised a procedure which has been adopted as a tentative method by the association. In this method the determination of chlorine is con-

[1] Published with the approval of the Director as Paper No. 277, Journal Series, Minnesota Agricultural Experiment Station.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 170.
[3] *J. Am. Chem. Soc.*, 1907, 29: 1503.
[4] *J. Ind. Eng. Chem.*, 1914, 6: 908.
[5] *Assoc. Official Agr. Chemists, Methods*, 1920, 169.

fined to the extracted fat. O. S. Rask, as Associate Referee on Cereal Foods, has simplified this method and subjected it to collaborative study. (See page 68.)

These quantitative methods are somewhat involved and time-consuming. It accordingly appeared desirable to develop, if possible, a more rapid technical method for determining the extent of treatment with chlorine. In addition, there were at least two other important phases that should be studied: First, the effect of chlorine treatment upon the electrolytic resistance of flour extracts, to ascertain whether such treatment would seriously affect the correlation previously determined by Bailey and Collatz[1] between the conductivity and flour grade; second, to determine the effect of chlorine bleaching upon the hydrogen ion concentration and buffer action of flour extracts, because of the significance of such values as discussed by Bailey and Peterson[2].

In the first series of studies two samples of natural hard-wheat flour were employed: (1) Patent, containing 0.43 per cent of ash; and (2) clear, containing 0.84 per cent of ash. These flours had already aged for several months and hence were somewhat less creamy than fresh hard-wheat flour. This is evident from the gasoline color values shown in Table 1. Six portions of each sample were bleached with the equivalent of 10, 20, 30, 40, 50 and 60 cc. of chlorine per 100 grams of flour, respectively. Ten grams of each portion, as well as the original natural flour, were then suspended in 100 cc. of water at 25°C. and maintained at that temperature for exactly 30 minutes. The mixture was shaken at frequent intervals during the extraction period to keep the flour particles in suspension, after which it was placed in a suitable glass vessel and whirled rapidly in a centrifuge for about 5 minutes to throw the particles out of suspension. A portion of the clear supernatant extract was then poured into a conductivity cell and its electrolytic resistance at 30°C. determined in the conventional manner. This method and the correlation between electrical conductivity and flour grade have been discussed in the paper by Bailey and Collatz previously referred to.

Another portion of each sample was mixed with water in the proportion of 1 gram of flour to 5 cc. of water at 25°C. and maintained at that temperature for exactly 60 minutes. The mixture was clarified by centrifuging and the hydrogen ion concentration determined electrometrically by means of the hydrogen electrode (described by Bailey[3]) connected through a calomel half-cell to a potentiometer. Results of these measurements are reported in terms of pH. In addition, the gasoline color values were determined, using the method of Winton[4].

---

[1] *J. Ind. Eng. Chem.*, 1921, **13**: 319.
[2] *Ibid.*, 916.
[3] *J. Am. Chem. Soc.*, 1920, **42**: 45.
[4] U. S. Bur. Chem. Bull. **137**: (1911).

From the data in Table 1 it appears that the specific conductivity increases fairly regularly with the quantity of chlorine used in bleaching. Thus bleaching the patent flour with 20 cc. of chlorine per 100 grams of flour, which is slightly more chlorine than is recommended for commercial bleaching, increased the conductivity of the water extracts 0.48 ($K_{30}x10^4$). This is equivalent to about 0.045 per cent of ash, when unbleached flours of varying ash content are compared. Bleaching the patent with 40 cc. of chlorine per 100 grams of flour increased the conductivity 1.13 units. If the ash content be known, it is probable that the extent of treatment with chlorine could be estimated by the deviation of the specific conductivity from the normal for flour of the same ash content. It is evident also that the ash content of flours treated with chlorine can not be accurately estimated from the conductivity alone unless the extent of treatment be known.

Hydrogen ion concentration is also increased appreciably by the chlorine treatment. Since the patent flour used in these studies was milled several months previously it followed that its initial pH was lower, and its hydrogen ion concentration accordingly higher than freshly milled flours of the same grade, which generally have a pH of about 6.0 to 6.1. Bleaching with 20 cc. per 100 grams of patent flour changed its hydrogen ion concentration through 0.34 units in terms of pH, while the clear grade flour, because of its higher buffer action, on similar

TABLE 1.

Effect of varying quantities of chlorine upon the specific conductivity and hydrogen ion concentration of patent and clear flour bleached in the laboratory.

CHLORINE USED PER 100 GRAMS OF FLOUR	GASOLINE COLOR VALUE	SPECIFIC CONDUCTIVITY OF WATER EXTRACT	pH
	Patent flour.		
cc.		K_{30} x 10^4	
0	0.72	5.51	5.51
10	0.70	5.70	5.33
20	0.58	5.99	5.17
30	0.53	6.21	5.00
40	0.53	6.64	4.77
50	0.52	7.06	4.60
60	0.52	7.40	4.43
	Clear flour.		
0	0.86	8.50	6.00
10	0.86	8.72	5.93
20	0.72	9.23	5.83
30	0.69	9.70	5.73
40	0.67	10.05	5.61
50	0.65	10.34	5.49
60	0.64	10.54	5.38

treatment changed pH only 0.17 units. Heavier dosages of chlorine further increased the hydrogen ion concentration.

To ascertain the effect of varying dosages of chlorine upon the buffer action of flour extracts, the procedure used by Bailey and Peterson was employed. To different portions of the 1 to 5 extract were added 0.02 hydrochloric acid and 0.02 sodium hydroxide in the proportions of 10, 20, 30, 40 and 50 cc. per 100 cc. of extract, respectively. The hydrogen ion concentration of each of these preparations was then determined and from these results, as given in Table 2, it appears that chlorine bleaching does effect an increase in the buffer action of water extracts. Possibly this is due to the increased hydrolysis of phytin in the presence of the hydrochloric acid resulting from the chlorine treatment. Certain products of such hydrolysis, notably phosphates, may constitute the buffers which manifest themselves on such treatment.

TABLE 2.

Hydrogen ion concentration (in terms of pH) on addition of 0.02 acid and alkali to water extracts of patent and clear flour.

Chlorine Used Per 100 Grams of Flour	0.02 N Hydrochloric Acid Added Per 100 cc. Extract					0.02 N Sodium Hydroxide Added Per 100 cc. Extract					
	50	40	30	20	10	0	10	20	30	40	50
cc.						*Patent flour.*					
0	2.54	2.69	2.93	3.36	4.14	5.51	6.96	8.52	9.33	10.06	10.43
10	2.50	2.65	2.93	3.31	4.06	5.33	6.93	8.39	9.47	9.97	10.41
20	2.52	2.67	2.92	3.31	4.04	5.17	6.90	8.33	9.42	9.96	10.35
40	2.62	2.76	3.03	3.40	3.94	4.77	5.83	6.95	8.11	8.55	9.72
60	2.63	2.77	3.03	3.33	3.80	4.43	5.22	6.22	7.08	8.15	9.09
						Clear flour.					
0	2.92	3.16	3.55	4.09	4.90	6.00	6.78	7.44	8.28	9.01	9.63
10	3.01	3.25	3.67	4.21	5.00	5.93	6.61	7.10	7.64	8.57	9.33
20	3.01	3.23	3.63	4.16	4.94	5.83	6.39	6.96	7.54	8.18	9.06
40	2.96	3.18	3.52	4.01	4.72	5.61	6.34	6.80	7.27	7.89	8.67

The flours discussed in the foregoing paragraphs were bleached on a small scale in the laboratory. It then appeared desirable to apply these tests to flours treated in a flour mill on a commercial scale. The Pillsbury Flour Mills Company kindly agreed to provide the material, and on the afternoon of August 4, 1921, a sample of unbleached patent flour was drawn from their packers. Immediately thereafter the chlorine was introduced into the agitator at the rate of one-half ounce per barrel of flour, and a sack of flour thus treated was drawn from the spout immediately below the bleaching agitator. Rask also supplied samples of the bleached and natural flour used in the determination of chlorine by his collaborators. The bleached sample of this pair had

been treated with chlorine at the rate of 14 ounces per 26 barrels of flour, or slightly more than was used in the Pillsbury mill.

Results of tests of these flours, given in Table 3, show that the commercially treated samples responded to chlorine treatment in essentially the same manner as did those bleached in the laboratory. These studies will be repeated in the Minnesota State Experimental Flour Mill as soon as the bleaching equipment is installed and ready to operate.

TABLE 3.

Effect of ordinary commercial bleaching with chlorine upon the specific conductivity and hydrogen ion concentration of flour.

SOURCE OF SAMPLE	DESCRIPTION	GASOLINE COLOR VALUE	SPECIFIC CONDUCTIVITY OF WATER EXTRACT	pH	ASH
			$K_{30} \times 10^4$		per cent
Rask	Unbleached	1.73	5.29	6.00	0.48
	Bleached	0.86	5.53	5.64	.
Pillsbury Mill	Unbleached	2.00	5.50	6.07	0.40
	Bleached	1.25	5.99	5.65	...

Winton called attention to the partial or entire disappearance of the nitrite reaction from flours bleached with nitrogen peroxide when stored for several months. It was accordingly deemed advisable to determine whether or not the differences in these physico-chemical constants were modified on extended storage. The pair of samples from the Pillsbury Mill was accordingly retained and tested at occasional intervals. A portion of each sample was stored in a tightly covered Mason jar, the remainder in an ordinary cotton flour sack. After two months of storage in this manner, as shown in Table 4, no appreciable change in conductivity had occurred, and the increase in hydrogen ion concentration was about the same in all cases. The pH of the natural or un-

TABLE 4.

Effect of storage in jars and sacks upon the conductivity and hydrogen ion concentration of patent flours.

SAMPLE	STORED IN—	SPECIFIC CONDUCTIVITY OF WATER EXTRACTS		pH OF WATER EXTRACTS	
		August 4, 1921	October 3, 1921	August 4, 1921	October 3, 1921
		$K_{30} \times 10^4$	$K_{30} \times 10^4$		
Unbleached..	Mason jar	5.48	5.50	6.07	5.92
	Cotton sack...	5.49	5.49	6.07	5.95
Bleached........	Mason jar....	6.00	6.01	5.65	5.48
	Cotton sack......	5.90	5.87	5.65	5.46

bleached flour had not reached that of the freshly bleached flour as yet, however. These samples will be retained, and this study extended over as long a time as possible.

SUMMARY.

Bleaching flour with chlorine increases the specific electrical conductivity, hydrogen ion concentration, and buffer action of flour extracts in direct ratio to the quantity of chlorine used.

These differences apparently do not disappear on storing the flour for several months.

QUANTITATIVE DETERMINATION OF CHLORINE IN BLEACHED AND NATURAL FLOURS.

By O. S. Rask (University of Minnesota, University Farm, St. Paul, Minn.), *Associate Referee.*

At the request of the Referee on Cereal Foods, the writer conducted a collaborative study of methods for the determination of the chlorine content of chlorine-bleached flours. Two methods, designated as Method I and Method II, were studied. Method I was proposed by the writer and Method II is given in Methods of Analysis[1] as the present tentative method. The materials used consisted of unbleached and chlorine-bleached portions of a hard-wheat patent flour milled in a commercial mill under the writer's supervision. The unbleached portion was taken on a Monday morning after the mill had been in operation about three hours and before the bleacher had been turned on. The chlorine bleacher was then turned on and the bleached portion taken about one hour later. Chlorine was applied at the rate of 14 ounces per 26 barrels of flour. So far as the writer is aware, this rate of application approximates that of average commercial practice in bleaching with chlorine.

Copies of Methods I and II, together with samples of the unbleached and chlorine-bleached flours, were sent to each collaborator. At the suggestion of certain cereal chemists, the collaborators were requested to give special consideration to Method I and to study Method II only if their time and other facilities permitted. For this reason several collaborators reported no results on Method II.

The methods are the following:

CHLORINE CONTENT OF CHLORINE-BLEACHED FLOUR.

REAGENTS.

(a) *Petroleum ether fractionated at 60–100°C.* (1).

(b) *Alkali solution.*—Dissolve 40 grams of sodium or potassium hydroxide in 1 liter of alcohol.

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 169.

(c) *Potassium chromate indicators.*—Dissolve 5 grams of potassium chromate in water, add a solution of silver nitrate until a slight red precipitate is produced, filter and dilute to 100 cc.

(d) *Dry C. P. calcium carbonate.*

(e) *Standard silver nitrate solution.*—Dissolve 4.791 grams of silver nitrate in water and dilute to 1 liter. 1 cc. is equivalent to 1 mg. of chlorine. Check by titration against standardized solution of sodium chloride.

DETERMINATION.

Method I.

Weigh 75 grams of the flour into a cork-stoppered bottle of suitable size and shape. Add, by means of a pipet, 150 cc. of the petroleum ether. Stopper tightly and shake vigorously for about 1 minute. After standing 1 hour, shake again until the flour has been loosened from the bottom of the flask. Set aside for 16 hours, preferably overnight. Shake once more until the flour has been loosened from the bottom of the flask. Allow to settle for a few minutes and then filter on a dry folded filter. The funnel should be covered with a watch glass during filtration in order to reduce evaporation. Collect the filtrate in a 100 cc. Erlenmeyer flask (2) and pipet 50 cc. into a nickel or platinum (3) dish of 80–90 cc. capacity. Add 5 cc. of the alkali solution and evaporate to dryness on a steam bath. Carefully char the contents of the dish over a Bunsen burner or in an electric muffle, preferably the latter. Extract the charred mass with 15–18 cc. of water, then once with an equal amount of dilute nitric acid (2 parts water and 1 part acid) and finally 2 or 3 times with water, all extracts being filtered through a 7 cm. filter paper and collected in a 300 cc. beaker or Erlenmeyer flask. Transfer the filter paper containing the charred residue to the dish and return same to the muffle and ignite contents to a white ash. Dissolve the ash in 5% nitric acid and add the solution to the filtrate previously obtained. Neutralize the acidity of the filtrate with a slight excess of dry calcium carbonate. Add 5 cc. of potassium chromate indicator solution and titrate with the standard silver nitrate solution. Prepare a blank containing the same amounts of all reagents used in the determination. As calcium carbonate labeled C. P. invariably contains appreciable amounts of chlorine a certain weighed quantity of this reagent should be used in the determination and the same amount in the blank. 2 to 2½ grams is usually sufficient. Correct for the amount of silver nitrate necessary to give in the blank, so prepared, the shade obtained at the end of the titration of the sample. Compute chlorides to parts per million.

Owing to the small amount of chlorides dealt with in this determination, special precautions must be taken that the air of the laboratory during the entire operation is not contaminated with chlorine or hydrochloric acid fumes and that all reagents employed are as free as possible from chlorine. The blank determination should be conducted simultaneously to ascertain the necessary corrections for conditions in the laboratory as well as chlorine content of reagents.

NOTES.

(1) A low boiling petroleum ether can not be used because of errors introduced through rapid evaporation.

(2) Filtrate may be collected directly in a 50 cc. volumetric flask if desired. Attention is called to the fact that such flasks are usually calibrated to contain and not to deliver the specified volume. Hence in transferring its contents to the dish it must be rinsed with additional portions of the solvent.

(3) Nickel dishes are usually prescribed for this kind of work on account of the corrosive action of chlorides on platinum. However, by following the above prescribed precautions, platinum may be used.

Method II.

Weigh 25 grams of flour into a flat-bottomed aluminum dish, 8–10 cm. in diameter, and dry 5 hours in a boiling water or steam oven; transfer, with as little exposure to the air as possible, to a continuous fat extractor and extract for 16 hours with anhydrous alcohol-free ether, which is also free from chlorine. Transfer the ether extract to a nickel or platinum dish and add 5 cc. of the alkali solution. From this point proceed as in Method I.

The results of the collaborators are compiled in the following table:

Determination of the chlorine content of chlorine-bleached flours.

(Results reported as parts per million)

ANALYST	METHOD I		METHOD II	
	Natural Flour	Bleached Flour	Natural Flour	Bleached Flour
J. A. Le Clerc, Minor-Hillard Co., Wilkes-barre, Pa.	4	100		.
T. H. Hopper, North Dakota Agricultural Experiment Station, Fargo, N. D.	None	60		..
C. B. Morison, American Institute of Baking, Chicago, Ill	25	106	.	..
E. L. Tague, Kansas Agricultural College, Manhattan, Kans	8	104	6	92
E. E. Smith, F. W. Stock & Sons, Hillsdale, Mich	20	76		.
C. H. Bailey, University of Minnesota, St. Paul, Minn	27	96	40	102
Emily Grewe, Federal Mill & Elevator Co., Lockport, N. Y	24	106	.	.
O. S. Rask	25	102	50	95
Average	16.6	93.7	32	96.3
D. J. Mayveety*, National Biscuit Co., New York, N. Y.	74	177	93	215
B. A. Dunbar*, South Dakota Agricultural College, Brookings, S. D.	52	86	49	128

*As these collaborators used a slightly different technique in correcting for the chlorine content of reagents used, their results were not included in computing the average.

DISCUSSION.

The work thus far has shown the necessity of making certain changes in the directions which apply to both methods. It has been found necessary to make the first extraction of the charred mass with acid instead of wat[illegible] in order to obtain a clear and colorless filtrate in which the subsequent colorimetric determination can be made. Apparently the carbon in this char fails to act as a decolorizing agent in an alkaline medium. It is recommended therefore that the sentence under Method I,

which reads as follows: "Extract the charred mass with 15–18 cc. of water then once with an equal amount of dilute nitric acid, etc.", be changed to read as follows: "Extract the charred mass with two successive 18–20 cc. portions of dilute nitric acid (one part acid to three parts water) being careful to avoid mechanical losses due to evolution of carbon dioxide. Then extract the mass two or three times with water, all extracts being filtered through a 7 cm. filter paper, etc."

Collaborators who used nickel dishes in which to char the extracts report the formation of a green nickel nitrate which interfered with the end point in the titration. It is further recommended, therefore, that directions be changed so as to specify the use of platinum dishes exclusively for charring the extracts.

A glance at the tabulated results of the collaborators will show the necessity of a continuation of this work before any definite recommendations can be made with regard to the value of either method. However, these results show that Method I is worthy of further consideration. As a technical method it is preferable to Method II owing to its simpler technique and the less expensive apparatus which it requires. It is recommended, therefore, that the above change be made in the directions and that the study of both methods, so changed, be continued to ascertain more completely their relative merits.

MICROSCOPIC METHOD FOR THE QUANTITATIVE DETERMINATION OF RICE HULLS IN RICE BRAN.

By B. H. SILBERBERG (Bureau of Chemistry, Washington, D. C.).

The Bureau of Chemistry has been using on official samples the microscopic method for the determination of rice hulls in rice bran[1] which was presented to the association last year by the Associate Referee on Stock Food Adulteration. The following table is compiled from results on record in the Bureau:

Rice hulls in rice bran.

SAMPLE NO.	CRUDE FIBER	HULLS ESTIMATED FROM CRUDE FIBER	HULLS DETERMINED BY MICROSCOPIC METHOD
	per cent	*per cent*	*per cent*
1	15.5	21	About 20
2	15.4	21	20–25
3	14.8	19	15–20
4	10.7	9	Not over 10
5	11.6	10	Less than 10

[1] *J. Assoc. Official Agr. Chemists*, 1921, 5: 77.

Since these results bear out the conclusions drawn last year from those submitted by collaborators, it is again recommended that the method be adopted by the association as a tentative one.

No report on the limit of accuracy in the determination of small amounts of alcohol in beers was made by the associate referee.

No report on vinegars was made by the referee.

No report on flavoring extracts was made by the referee.

REPORT ON MEAT AND MEAT PRODUCTS.

By C. ROBERT MOULTON (Agricultural Experiment Station, Columbia, Mo.), *Referee.*

In accordance with the recommendations adopted last year a further study was made of the ferrous chloride method for nitrates and nitrites (calculated as sodium nitrate) and the method for sugar in meat.

The referee secured the assistance of nine collaborators, but some of these were unable to make reports.

The material used—lean, ground, air-dry, fresh beef—was prepared by Ralph Hoagland, of the Bureau of Animal Industry, Washington, D. C. The total sample weighed 1390 grams. Thirty-five grams of C. P. dextrose and 7 grams of C. P. potassium nitrate were dissolved in water and sprayed over the spread-out sample. After thorough mixing the material was again spread out thinly on glass trays, stacked one above the other, and dried by a current of air at room temperature. When dry, the sample, weighing now 1455 grams, was again well mixed and placed in glass sample jars provided with rubber gaskets and clamps. If the chemicals added were dry and pure the sample would have contained 2.40 per cent of dextrose and 0.402 per cent of nitrate calculated as *sodium nitrate*. About 150 grams were sent to each collaborator, with the advice to keep the sample sealed when not in use so as to prevent the taking up of moisture from the air by this hygroscopic material.

ESTIMATION OF TOTAL SUGAR IN MEATS.

Directions were given that the methods as outlined in the Book of Methods[1] be followed. Twenty grams of the dried meat was recommended as equivalent to 100 grams of fresh meat. As an alternate method of extraction the following was offered:

Weigh out the meat into an 800 cc. beaker, add 400 cc. of water and gently heat to boiling. Continue boiling for about 30 minutes, transfer the mixture to a 1000 cc. volumetric flask, cool and fill to the mark with water. Mix, filter and evaporate 800 cc. of the solution in the usual manner.

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 213.

The results shown in Table 1 were obtained in the chemical laboratory of Swift & Company, Chicago, Ill.

TABLE 1.

Estimation of dextrose in dried meat.

CUPROUS OXIDE METHOD	ELECTROLYTIC METHOD	THIOSULFATE METHOD
per cent	*per cent*	*per cent*
1.06	1.018	1.018
1.01	0.980	0.980
0.962	0.914	0.903
1.018	1.020	1.006
0.928	0.928	0.906

The following comments were offered with the report:

The three determinations shown in Table 1 were made on the same sample and in the order given, consequently any errors made on the cuprous oxide and electrolytic methods are cumulative in the thiosulfate method. We prefer the electrolytic method because we believe there is less chance of error in it. We have the following suggestion to offer: After evaporating the extract to 25 cc. filter it as it is transferred to the 100 cc. flask. This would remove an appreciable amount of organic matter that separates out on evaporation and would diminish the bulky phosphotungstic precipitate.

C. H. Robinson, Central Experimental Farm, Ottawa, Canada, obtained the results shown in Table 2. He reported a water content of 8.54 per cent in vacuo at 80°C.

TABLE 2.

Total sugar in meats.

(Calculated as dextrose.)

I.	First method of extraction:	
	Percentage of dextrose	A–0.51
		B–0.50
II.	Alternate method of extraction:	
	Percentage of dextrose	A–0.48
		B–0.46

Comments by Robinson.—Dextrose in every case was determined by the cuprous chloride-iodine method[1], checked against a commercially pure dextrose. This method is in general use in the laboratory for similar determinations such as starch in sausages. I had intended to check these results by the official Munson and Walker method[2] but the sample ran out before this could be done. Better results were obtained by removing the excess of phosphotungstic acid by powdered potassium chloride before instead of subsequent to inversion, as outlined in methods of determinations.

Hoagland reported 0.39, 0.37 and 0.38 per cent of sugar as dextrose. He found that the precipitation of phosphotungstic acid occurred more readily when the solution was not neutralized. His comments follow:

The sugar was estimated by the method supplied with some modification. After inversion of the sugar in the clarified extract, the method states that the solution should be cooled, neutralized to litmus, made to volume, filtered and that potassium chloride

[1] *J. Ind. Eng. Chem.*, 1919, **11**: 747.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 78.

should be added to the filtrate to precipitate any excess of phosphotungstic acid present. On following this procedure I found that the precipitation took place slowly and incompletely. However, on adding a little concentrated hydrochloric acid, a heavy precipitate formed and complete precipitation was obtained. I then adopted the following procedure: After inversion of the clarified extract, cool, but do not neutralize the acid, and make to volume. Filter if necessary, add dry potassium chloride to precipitate excess of phosphotungstic acid, filter and test for complete precipitation. Take an aliquot portion of the filtrate, neutralize to litmus, make up to a given volume and take an aliquot portion for the determination of sugar. Good results were obtained by this procedure, the reduction of the Fehling's solution being normal. The reduced copper was estimated by Low's method since we commonly use this method.

Since the meat contained about 2.4 per cent of added dextrose and the collaborators found only about 1.0, 0.5 and 0.38 per cent it seems to be inconsequential that neither the original dextrose in the meat nor the purity of the added dextrose was determined. That the difficulty was not due to differences in the samples is shown by the reports on nitrates which follow.

It is to be regretted that more reports were not received. More work on the method is demanded.

NITRATES AND NITRITES (CALCULATED AS SODIUM NITRATE).

Ferrous Chloride Method.

The material described previously was used for this work. The collaborators were asked to follow the procedure given in the Book of Methods[1]. Sodium hydroxide replaced potassium hydroxide, and the use of the pinch-cock was not recommended since it leads to difficulties.

Instead of calculating the nitrate from the observed volume of gas the following standard sodium nitrate solution was recommended:

Dissolve 2 grams of C. P. sodium nitrate in 1 liter of recently boiled distilled water. Take 50 cc. (equivalent to 0.1 gram sodium nitrate) and determine the amount of nitric oxide. 0.1 gram of sodium nitrate should give 26.36 cc. of nitric oxide at 0°C. and 760 mm. pressure. Calculate the percentage of sodium nitrate from the volume of nitric oxide obtained from the sample with the volume obtained from 0.1 gram C. P. sodium nitrate, both being measured at room temperature. This is conveniently done by transferring the measuring tube to a tall jar containing 40% sodium hydroxide solution (commercial). The temperature of the surrounding caustic solution will soon (10–15 minutes) be imparted to the contents of the tube, and the volume of nitric oxide is read with the tube in such a position that the level of the solution within and without the tube coincide. The caustic in the jar should be kept at room temperature.

NOTE.—A single coil of tin tubing fitted into the trough and carrying a current of cold water during the determination greatly facilitates the operation. After all the air has apparently been driven out of the apparatus, always boil a short time longer after the delivery tube has been placed under the eudiometer to make certain that no air remains. Next gradually introduce a measured portion of standard nitrate solution, rinse the funnel tube with 10 per cent of hydrochloric acid and boil until all nitric oxide has been driven over. After the gas tube has been removed quickly invert another tube over the delivery tube and boil a short time longer to make sure that all nitric oxide has been driven over. Another portion of the standard solution is run into the apparatus and the determination is repeated as above. Then run the samples in the same way in each case making certain that all the nitric oxide has been driven over. After running 6 or 8 determinations, not counting the standards, finally run another standard. The three standards should check within 0.5 and about 35 cc.

The following results were reported:

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 210.

TABLE 3.

Nitrates in dried meat.

ANALYST	SODIUM NITRATE	AVERAGE
	per cent	*per cent*
Chemical Laboratory, Swift & Co., Chicago, Ill.	0.400 0.421 0.407	0.409
C. H. Robinson.	0.373 0.382 0.389	0.382
A. L. Mehring, Bureau of Animal Industry, Washington, D. C.	0.332 0.319 0.321	0.324
Ralph Hoagland.	0.39 0.42 0.41	0.407
Added nitrate.		0.402

Robinson reported that he calculated the nitrate by comparison with the gas evolved from 0.1 gram of sodium nitrate. The results from two other collaborators were probably calculated in the same manner according to the directions although no statement was made by them.

Hoagland reported as follows:

The nitrates were determined by the method furnished except for slight modification. Instead of extracting the meat several times with hot water, it was boiled with about 500 cc. of water, transferred to a liter flask, and when cool the solution was made to volume. The contents of the flask were filtered and 850 cc. of the filtrate were evaporated to about 30 cc. and used for the determination.

The results of three of the four analysts show a recovery of 100, 100 and 95 per cent of the added nitrate. This speaks well for the method and shows the advisability of using a standard sodium nitrate solution for calculating the nitrates in the sample under investigation.

The report of the associate referee for 1919[1] showed that 82.6 per cent of the added sodium nitrate was recovered by comparison with a standard nitrate solution while only 69.4 per cent was recovered by calculating from the volume of gas alone.

The modified procedure outlined by Mitchell and given in the 1919 report seems to give more accurate results and to be safer.

RECOMMENDATIONS.

It is recommended—

(1) That the method for sugar in meats receive further study.

[1] *J. Assoc. Official Agr. Chemists*, 1921, **4**: 505.

(2) That the method outlined for the determination of nitrates in meat products be adopted in place of, or as a modification of, the present tentative method.

THE SEPARATION OF MEAT PROTEINS.

By C. Robert Moulton (Agricultural Experiment Station, Columbia, Mo.), *Associate Referee*[1].

The Official and Tentative Methods of Analysis of the A. O. A. C. permit the determination of a few protein groups in meat and its products. The soluble nitrogenous matter can be divided into coagulable protein (globulin and albumin), proteose, peptone and gelatine, and meat bases. In an attempt to extend these methods to allow a further subdivision of the soluble nitrogenous matter the methods used by Grindley[2] at the University of Illinois and extended by Trowbridge at the University of Missouri have been used and further amplified. These methods permit the subdivision of the soluble nitrogenous matter into soluble protein, coagulable protein, proteose, peptone and peptid, and amino acid and extractive nitrogen. This gives one more group than permitted by the official methods.

The first attempt at extension was to apply well-known principles to the separation so as to allow the determination of globulin and albumin as separate fractions. The water-soluble, heat-coagulable proteins consist of a mixture of globulin and albumin. Pure water will dissolve albumins but not globulins[3]. However, when pure water is added to raw meat a dilute salt solution results owing to the solubility of the phosphates of potassium and smaller amounts of other salts of potassium and sodium. This salt solution will dissolve some globulin. Heat will coagulate both the globulin and albumin. The globulins can be removed by half saturating their solutions with ammonium sulfate. Some can be salted out by saturating with sodium chloride. Other salts may also be used.

PREPARATION OF THE EXTRACT.

A cold water extract of the raw meat is prepared according to **XX, 24**[4]. In the laboratories of the Department of Agricultural Chemistry of the University of Missouri a total of 150 or 180 grams of fresh meat is about equally divided among twenty beakers of 150 cc. capacity, and one washing with 50 cc. of cold water and eight with 25 cc. are employed. All the washings are collected and made up to some convenient volume —six liters. This extract is used for analysis.

---

[1] C. F. Ahmann and W. S. Ritchie of the Department of Agricultural Chemistry, University of Missouri, collaborated with the associate referee in this work. The data presented were used by Ahmann in his dissertation for the degree of Master of Arts at the University of Missouri. The interpretation and emphasis in this report differ in some essentials from those in the thesis.

[2] *J. Am. Chem. Soc.*, 1904, 26: 1086; 1905, 27: 658; 1906, 28: 25, 469.

[3] There is a water-soluble pseudo-globulin in ox serum and there may be examples in other tissues. See Haslam, H. C. *Biochem. J.*, 1913, 7: 492.

[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 214.

GLOBULIN.

Several 100 cc. aliquots of the extract prepared as directed are placed in 250 cc. (or 400 cc.) beakers and 100 cc. of cold saturated zinc sulfate ($ZnSo_4 . 7H_2O$) solution are added to each. After mixing, the solutions are allowed to stand in a cold room until separation occurs. Under the conditions outlined a good separation occurs in 48 hours. The solutions are then filtered onto filter papers fitted and wet with half-saturated zinc sulfate solution. The coagulum is washed with cold half-saturated zinc sulfate solution. Three washings of 20 to 25 cc. were used on account of the slow filtration. Coagula fairly free from mother liquor are thus obtained. The nitrogen was determined by the Kjeldahl-Gunning-Arnold method[1].

In Table 1 are shown the results on four samples of lean round steak of beef and two of pigeon flesh. The results, expressed as per cent nitrogen in fresh meat, in many cases show uniformity. In others the agreement is not so good as is desired. Sample 20 was the first one tried and both the method and the manipulator were new. Two out of the other 25 results are excluded from their respective averages since they are much higher than the companion results. The method seems to give sufficiently good agreement for comparative purposes.

TABLE 1.

Globulin nitrogen in flesh.

(Percentage of total flesh.)

SAMPLE	BEEF 20	BEEF 26	BEEF 104	BEEF 9	PIGEON 78	SQUAB 88
1	0.168	0.123	0.172*	.	0.208	0.112
2	0.143	0.113	0.131	0.394	0.214	0.112
3	0.134	0.135	0.151	0.395	0.228	0.117
4	...	.	0.137	0.400	0.214	0.141*
5	. .	.	0.134	0.404	0.211	0.129
6	.....	.	. .	0.400	0.208	0.102
Average	0.148	0.124	0.138	0.399	0.214	0.114

* Omitted from average.

The effect of saturated sodium chloride on the coagulation of globulin was next studied. Beef Sample 9 was used. When the calculated amount of the salt was added but two-thirds of the globulin coagulated by half-saturated zinc sulfate was thrown down. Table 2 shows the results. Two samples, marked with asterisk, were treated with quite an excess of sodium chloride, and the globulin coagulated was increased about 20 per cent but still remained considerably below the amount coagulated by half-saturated zinc sulfate.

It was thought that perhaps the ratio of the salt to the amount of material to be precipitated might affect the results obtained. Consequently aliquots of the extract were taken and diluted with an equal volume of cold water. Then they were treated with the two salts as

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 7.

TABLE 2.

Zinc sulfate vs. sodium chloride for globulin nitrogen.

Half-Saturated Zinc Sulfate		Saturated Sodium Chloride	
Concentrated Extract	Dilute Extract	Concentrated Extract	Dilute Extract
0.394	0.409	0.252	0.200
0.395	0.344	0.246	0.199
0.400	0.377	0.252	0.168†
0.404	. .	0.318*	0.187
0.400	. .	0.314*	0.200
Average 0.399	0.377	0.260	0.197

*Omitted from above average Large excess of sodium chloride
†Omitted from the average.

before. The results are shown in Table 2. In both cases a smaller quantity of material was coagulated than when the undiluted extract had been used, although the concentration of salt was the same as in the undiluted extracts.

Dilution of the extract or the use of sodium chloride to saturation does not remove as much nitrogen, classed as globulin, as is removed on half saturating the undiluted extract with zinc sulfate.

This water extract was acid to both litmus and phenolphthalein and so the pH was probably on the acid side of the iso-electric point of the proteins in solution. Consequently the anion of the salt used was prepotent over the cation[1] in forming combinations with the protein. The sulfate would therefore be a better coagulant (or precipitant) than the chloride as has been shown by Lewith, Hofmeister, Pauli and others and quoted by Robertson[2]. Chick and Martin[3] have shown that diluting a solution of egg-albumin allowed the same concentration of ammonium sulfate to precipitate not only a smaller quantity of the protein but a smaller proportion of the total.

The amounts of globulin are in all cases probably too low. Both Haslam[4] and Mellanby[5] have shown that zinc sulfate is not so good a precipitating agent as ammonium or sodium sulfates. On the other hand it must be emphasized that not globulin alone is precipitated (coagulated) under the conditions given. Some albumin will be thrown down also.

ALBUMIN.

The filtrates from the globulin determination were coagulated by heat in an attempt to coagulate the albumin remaining in solution. In

[1] For the theory and facts on which it is dependent the reader is referred to the recent work of Loeb. *J. General Physiol.*, 1918–19, 1: 39, 237, 363, 483, 559.
[2] The Physical Chemistry of the Proteins, 1918, 107–134.
[3] The Precipitation of Egg-albumin by Ammonium Sulfate. A contribution to the theory of the salting out of proteins. *Biochem. J.*, 1913, 7: 380.
[4] *J. Physiol.*, 1907–8, 36: 164.
[5] *Ibid.*, 288.

all cases the coagulum obtained was very small in amount representing only from 0.050 to 0.098 per cent of the meat as albumin nitrogen. From results shown it will be seen that these figures are much too low. A few of the later filtrates were examined for acidity, since it was thought that perhaps the albumin failed to coagulate, owing to high acidity of the liquid which might have developed on standing, and coagulation of the globulin. Some of these required 54.5 cc. of normal sodium bicarbonate solution to neutralize them, using phenolphthalein as an indicator. Heat coagulation of the neutralized filtrate from the globulin determination gave no better results. The salt solution in some manner other than aiding in increasing the acidity prevents the heat coagulation of the albumin.

The albumin nitrogen can be determined indirectly by subtracting the globulin nitrogen from the nitrogen obtained on coagulating the water extracts by means of heat. In this work the extracts were neutralized while on the steam bath by adding an excess of moist, freshly precipitated magnesium carbonate. This method has been used in the referee's laboratories for some time and has been considered very satisfactory. The percentage of the meat obtained as heat-coagulable nitrogen is shown in Table 3. Again Sample 20 does not give uniform results, due, probably, to the lack of experience on the part of the operator. Two of the six results for Sample 104 are at wide variance with

TABLE 3.

Heat coagulable nitrogen in flesh.

(Percentage of total flesh.)

BEEF 20	BEEF 26	BEEF 104	BEEF 9	PIGEON 78	SQUAB 88
0.321	0.381	0.379*	0.536	0.428	0.229
0.316	0.362	0.493	0.550	0.438	0.232
0.312	0.386	0.523	0.533	0.443	0.225
0.287	0.370	0.496	0.539	0.469	0.219
0.282	0.378	0.333*	0.529	0.433	0.248
0.282	0.378	0.454	0.536	0.441	0.202
0.304	0.375	.	.	0.441	0.223
0.299	0.385	.	.	0.455	0.215
0.303	0.385	.	. .	0.501	0.201
. ..	.	..	.	0.410	0.215
...	.	.	. .	0.471	0.221
...	.	. .	. .	0.453	0.221
. .	.	.	.	0.414	0.215
. .	.	. .	.	0.452	0.217
...	.	. .	..	0.407	0.186*
....	.	. .	.	0.436	0.232
.....	..	. .	.. .	0.448	0.226
... .	...	. .	. .	0.466	0.216
....	..	.	.	0.445	0.222
.....	...	....	...	0.424	0.219
Average 0.301	0.377	0.492	0.537	0.442	0.223

*Omitted from average.

the others. In general fairly good agreement is shown between the aliquots of the same extract.

In Table 4 is shown the calculation of the albumin nitrogen. The average results shown in Table 1 and Table 3 are used. Comparison of the different samples is of little value except to show the differences in composition of commercial samples of beef round. In half of the six samples the albumin and globulin were about equally divided. In two cases the albumin was much the larger, while only in one case was the globulin the larger.

TABLE 4.

Albumin nitrogen in flesh.

SAMPLE	BEEF 20	BEEF 26	BEEF 104	BEEF 9	PIGEON 78	SQUAB 88
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Globulin and albumin...	0.301	0.377	0.492	0.537	0.442	0.223
Globulin	0.148	0.124	0.138	0.399	0.214	0.114
Albumin by difference...	0.153	0.253	0.354	0.138	0.228	0.109

PROTEOSE.

The filtrates and washings from the heat-coagulable protein were concentrated to a volume of about 25 cc. They were then saturated with zinc sulfate ($ZnSO_4 . 7H_2O$) when cool and acidified with acid. Different quantities of acid were used with some of the extracts and in one case acetic acid was used. Table 5 shows the results obtained expressed as percentage of proteose nitrogen in the meat sample. It is seen that a larger quantity of acid added increased the proteose nitrogen precipitated by saturated zinc sulfate.

TABLE 5.

Influence of acidity on the precipitation of proteose by zinc sulfate.

SAMPLE	NO ACID	ACETIC ACID	SULFURIC ACID			
		5 cc. 2N	2.5 cc. 2N	5 cc. 2N	7.5 cc. 2N	1 cc. 1 to 1
20	0.000	.....	.....	....	.....	0.020
26	.....	0.012	.....	0.019	.....	.....
78	.....	.....	0.030	0.037	0.027	.....
88	....	.....	0.019	0.024	0.031	.....

In Table 6 are shown the results for all samples expressed in the usual terms. The quantity of proteose nitrogen is exceedingly small and this determination might well be omitted. It serves in this study,

TABLE 6.
Proteose nitrogen in beef and pigeon flesh.
(Percentage of total flesh.)

	BEEF 20	BEEF 26	BEEF 104	BEEF 9	PIGEON 78	SQUAB 88
	0.017	.....	0.030	0.017	0.042	0.023
	0.015	0.012	0.014	0.023	0.035	0.039
	0.028	0.027	0.023	0.023	0.035	0.031
	.....	.....	0.023	0.020	.....	...
	.....	.....	0.065*	..	...	...
	.....	.....	0.029	0.017	....	....
Average	0.020	0.019	0.024	0.020	0.037	0.031

*Omitted from average.

however, as a means of checking other determinations. These results are probably lower than would have been obtained with ammonium sulfate[1].

GLOBULIN, ALBUMIN AND PROTEOSE.

Several 100 cc. aliquots of the water extract were saturated with zinc sulfate ($ZnSO_4 . 7H_2O$) and acidified. This treatment should have thrown down globulin, albumin and proteose (albumose). Various amounts of sulfuric acid were tried and in one case acetic acid was used. The weight of sample varied from 2.25 to 3.00 grams and the percentage of nitrogen coagulated varied from 0.256 to 0.516. In Table 7 are shown the detailed results. This study of the effects of acidity was rather incidental to the work since the samples were used mainly for another purpose. There are consequently many gaps in the data. The values of 9, 18, 27 and 45 cc. of 2N sulfuric acid are the equivalents of 1, 2, 3 and 5 cc. of 1 to 1 sulfuric acid. These small amounts of more concentrated acid were used for the higher acidities in order not to dilute the 100 cc. of water extract unduly.

There is apparent a relation between the percentage of nitrogen precipitated and the acidity of the solution. For example, in Sample 88 an acidity given by 5 cc. of 2N acid coagulated 0.263 per cent of nitrogen which was complete as shown by the percentage on the bottom line of the table. This is the sum of the proteose nitrogen and the heat coagulated nitrogen. For Sample 20 an acidity of 9 cc. of 2N acid coagulated 0.330 per cent, i. e. it was sufficient for complete coagulation. For Sample 104 the lower concentrations of acid precipitated too small an amount of protein. However, 45 cc. of 2N acid gave complete coagulation, i. e. 0.516 per cent.

With Sample 26 low concentrations of acid gave incomplete coagulation, but sulfuric acid was better than acetic acid. With Sample 78

[1] Haslam, H. C., *J. Physiol.*, 1907–8, 36: 164.

the amount of acid in no case was great enough to give complete coagulation.

TABLE 7.

Protein coagulated with saturated zinc sulfate with varying acidities.

(Per cent nitrogen of fresh sample.)

ACID USED	SQUAB 88	BEEF 20	BEEF 26	PIGEON 78	BEEF 104
1¼ cc. of 2N acetic acid.	....	....	0.307 0.313 0.313	....	....
1¼ cc. of 2N sulfuric acid.	.. ..	... .	0.342 0.336 0.334	....	0.169 0.473 0.485
2½ cc. of 2N sulfuric acid.	... .	... .	... .	0.438 0.438 0.438	0.485 0.498 0.501
5	0.256 0.272 0.260	... .	... ...	0.445 0.421 0.442	0.501 0.452 0.449
9–10	0.231 0.178* 0.272	0.329 0.329 0.332	. ...	.... 0.445 0.421	0.503 0.481 0.487
15–18	0.256 0.239 0.260	... ...	... .	0.445 0.424 0.428	0.478 0.501 0.471
27	....	....	....	... ...	0.478 0.501 0.501
45	....	....	....	....	0.514 0.504* 0.517
Amount present that should have been coagulated..	0.254	0.321	0.396	0.479	0.516

*Omit from average.

In Fig. 1 are plotted the milligrams of nitrogen coagulated by zinc sulfate at saturation with the concentrations of acid added as abscissae. The three samples that gave complete coagulation lie on a straight line. For the two cases of incomplete coagulation the weight of protein (nitrogen) coagulated by a given concentration of acid was larger than the curve shows for complete coagulation. The weight that should have been coagulated is shown above the first point, and the concentration of acid probably needed for complete coagulation is shown by projecting this last point until it strikes the line. It should thus have taken a little over 3 cc. of 1 to 1 sulfuric acid to give complete coagulation in Sample 26 and about 4.5 cc. for Sample 78.

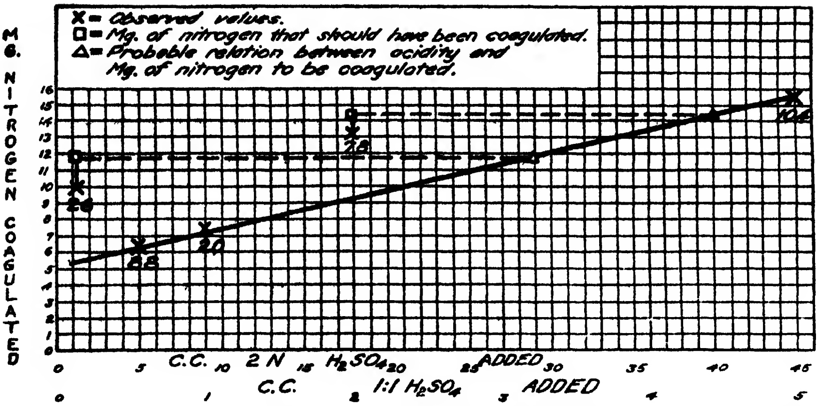


FIG. 1.—THE RELATION BETWEEN THE CONCENTRATION OF ACID AND THE QUANTITY OF PROTEIN COAGULATED BY SATURATED ZINC SULFATE.

Haslam has shown that the addition of acid to zinc sulfate is necessary in the separation of albumoses. The results given in this paper indicate that there is probably also a relation between the protein (globulin, albumin, and proteose) to be coagulated and the acidity of the solution. It is known that acid increases the precipitating power of salts. To what extent this is true in this case is shown by the following results with Sample 20 (Table 8) where the globulin fraction is increased from 0.148 to 0.269 per cent by the addition of 1 cc. of 1 to 1 sulfuric acid. The total globulin, albumin and proteose was but 0.330 per cent.

TABLE 8.

Effect of acid on the globulin fraction.

(Per cent nitrogen of fresh sample.)

ZINC SULFATE		
HALF SATURATED	HALF SATURATED ACIDIFIED	SATURATED ACIDIFIED
0.168	0.273	0.329
0.143	0.264	0.329
0.134	0.269	0.332

The concentration of the proteins to be coagulated has an effect on the total amount coagulated. The filtrates from the globulin determination for Sample 26 were saved, saturated with zinc sulfate and acidified with the equivalent of 1¼ cc. of 2N acid. Albumin and proteose should have been coagulated. The percentage of nitrogen thrown down was, however, only 0.169 when the difference between the globulin, albumin and proteose combined and the globulin fraction is 0.123 per

cent. Similar results occurred in the globulin determination when the water extract was diluted before adding the salt.

AMINO ACIDS AND EXTRACTIVES.

The fraction known as amino acids and extractives is sometimes called "rest" nitrogen and sometimes "meat bases". It is the fraction not precipitated by salt and tannic acid.

In this work an attempt was made to treat original aliquots of the water extract with salt and tannic acid as well as filtrates from the heat-coagulable protein. In nearly all cases difficulty was experienced in getting triplicate determinations to agree. The water extract, or the concentrated filtrate and washings from the coagulable protein determination, were placed in volumetric flasks of 100 cc. (or 200 cc.) capacity and 15 grams (30 grams for 200 cc.) of salt were added. This did not dissolve readily and the manipulator in many cases added the 30 cc. (60 cc. for the larger flask) of 24 per cent tannic acid before all the salt had dissolved. Even where solution was practically complete a difference in color of the mixtures was noticed on settling. The rapidity of addition and the method of mixing seemed to affect the color. Another difficulty experienced was to get the manipulator to use enough alkali during distillation to more than neutralize the larger amount of sulfuric acid required during the digestion.

It made no difference whether the original extract or the filtrate and washings from the coagulable protein was used. The detailed figures will not be given.

TABLE 9.

Distribution of nitrogenous bodies in raw meat.

(Expressed as nitrogen in percentage of meat.)

SAMPLE	BEEF 20	BEEF 26	BEEF 104	BEEF 9	PIGEON 78	SQUAB 88
Total nitrogen	3.150	3.579	4.079	3.350	3.466	3.794
Water soluble nitrogen	0.699	0.994	0.876	0.777	0.795	0.563
Heat coagulable nitrogen	0.301	0.377	0.492	0.537	0.442	0.223
Proteose nitrogen	0.020	0.019	0.024	0.020	0.037	0.031
Sum of above two	0.321	0.396	0.516	0.558	0.479	0.254
Globulin. albumin and proteose	0.330	*	0.516	†	*	0.256
Globulin nitrogen	0.148	0.124	0.138	0.399	0.214	0.114
Albumin nitrogen	0.153	0.253	0.354	0.138	0.228	0.109
Amino acid and extractive N	0.315	0.233	0.360	0.313	0.273	0.198
Peptone and peptid nitrogen ‡	0.062	0.165			0.043	0.111

* Lower than sum of heat coagulable and proteose nitrogen.
† Not determined. ‡ Determined by difference.

SUMMARY OF ANALYTICAL RESULTS.

In Table 9 are collected the summarized data for all the samples. Some few results are omitted because of obvious error or because the determination had not been made.

GENERAL SUMMARY.

The nitrogen of meat soluble in cold water is divided according to the methods of separation here employed approximately into globulin, albumin, proteose, peptone and peptid, and amino acid and extractive nitrogen.

Zinc sulfate at half saturation coagulates more nitrogen as globulin than does sodium chloride at saturation. Diluting the extract reduces the amount of nitrogen coagulated.

Globulin and albumin nitrogen are readily coagulated by heat in the presence of an excess of moist freshly precipitated magnesium carbonate.

Globulin, albumin and proteose nitrogen are coagulated by saturated zinc sulfate ($ZnSO_4 . 7H_2O$) when sufficiently acidified with sulfuric acid. Seven milligrams, or less, of nitrogen to be coagulated require 1 cc. of 1 to 1 sulfuric acid for complete coagulation; 12 milligrams require at least 3⅓ cc. and 15 milligrams require about 5 cc. The necessary amount of acid can be estimated from Fig. 1. Dilution of the extract resulting from a previous removal of globulin gives a smaller recovery in this fraction by an amount considerably greater than the globulin removed.

Difficulty was experienced in determining the amino acid and extractive nitrogen by coagulating the other fractions with tannic acid and sodium chloride. The method needs further study.

No claim is made that the fractions designated by specific names are pure. It is recognized that contamination may be great, but the results should nevertheless be of qualitative value.

Work will be continued along this general line. Zinc sulfate will be compared with ammonium sulfate.

RECOMMENDATIONS.

It is recommended—

(1) That further work be done concerning the relation of the concentration of acid and protein to the coagulation by salts of proteins of meat soluble in cold water.

(2) That zinc sulfate be compared with ammonium and sodium sulfates.

(3) That further work be done with the sodium chloride and tannic acid method to determine all the conditions necessary to give comparable results.

THE AMINO ACIDS IN THE GLOBULIN-ALBUMIN FRACTION OF BEEF FLESH.

By C. Robert Moulton (Agricultural Experiment Station, Columbia, Mo.), *Associate Referee*[1].

Three samples of the water-soluble, heat-coagulable proteins from the lean of the round cut of three beef steers were used in this work. These samples included the albumins and part of the globulins in the flesh and did not represent a single pure protein. Nevertheless the amino acid make-up of this fraction is of value, e. g. in questions affecting the nutrition of the animal.

The methods used were in general those devised by Van Slyke[2]. They are given with modifications below:

HYDROLYSIS[3].

Three grams of protein, in duplicate, were placed in 250 cc. Erlenmeyer flasks, to which 100 cc. of 3N hydrochloric acid were added. The flasks were placed in a water bath at 100°C. and allowed to remain until the protein was completely dissolved, when they were placed in an autoclave at 150°C. for 1½ hours. At the end of this time the hydrolysis was considered to be complete.

TOTAL NITROGEN.

The hydrolyzed material was washed into a 250 cc. Claissen distilling flask and concentrated in vacuo, driving off all the hydrochloric acid possible. The concentrate was then taken up with hot water, transferred to a 100 cc. graduated flask, cooled and made up to the mark. An aliquot of 5 cc. was taken for the total nitrogen determination, the Kjeldahl-Gunning-Arnold method[4] being used.

ACID-INSOLUBLE HUMIN[5].

The remaining 95 cc. were filtered and washed till free from chlorides. The nitrogen content of the black residue was determined by the Kjeldahl-Gunning-Arnold method.

AMMONIA (AMIDE) NITROGEN.

The filtrate from the acid-insoluble nitrogen determination was transferred to a liter Claissen distilling flask; 100 cc. of alcohol were added to prevent frothing and also a slight excess of a 10 per cent suspension of calcium hydroxide, as shown by the alkaline reaction and by the turbidity of the solution. The flask was placed in a water bath at 40°–50°C. and connected with two trap flasks containing N/14 hydrochloric acid and a few drops of methyl red and distilled at less than 30 mm. pressure for one-half hour. The acid from both trap flasks was transferred to a wide-mouth 500 cc. Florence flask and titrated with N/14 ammonia. The amount of hydrochloric acid neutralized by the ammonia distillate is found by difference.

---

[1] E. G. Sieveking of the Department of Agricultural Chemistry, University of Missouri, collaborated with the associate referee. This work forms a part of the dissertation presented by him for the degree of Master of Arts at the University of Missouri.

[2] *J. Biol. Chem.*, 1911, **10**: 15; 1915, **22**: 281.

[3] Van Slyke, D. D., *J. Biol. Chem.*, 1912, **12**: 295.

[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 7 .

[5] Gortner, R. A., and Holm, G. E., *J. Am. Chem. Soc.* 1917, **39**: 2477.

ACID-SOLUBLE HUMIN[1].

The solution and precipitate from the ammonia determination were filtered and washed free from chlorides and the nitrogen content of the precipitate determined by the Kjeldahl-Gunning-Arnold method.

PRECIPITATION AND WASHING OF THE PHOSPHOTUNGSTIC ACID PRECIPITATE.

The filtrate from the acid-soluble humin determination was returned to the liter Claissen distilling flask, acidified with hydrochloric acid, concentrated to about 100 cc. and washed into a 250 cc. Erlenmeyer flask. Then 18 cc. of concentrated hydrochloric acid and 15 grams of phosphotungstic acid, purified as described by Winterstein[2], were added. It was then diluted to 200 cc. and heated on a steam bath till practically all of the precipitate had dissolved. The precipitate was allowed to stand for 48 hours or more.

The solution and precipitate were poured onto a 2-inch Büchner funnel and washed until free from calcium with successive portions of from 10–15 cc. of a wash solution containing 2.5 grams of phosphotungstic acid and 3.5 grams of concentrated hydrochloric acid per 100 cc. and cooled to nearly 0°C. The test for calcium was made by allowing a drop or two of the solution from the Büchner to run down the side of a test tube containing about 5 cc. of an alkaline oxalate solution. If calcium were present the solution became turbid after standing a few minutes.

DECOMPOSING THE PHOSPHOTUNGSTATE PRECIPITATE AND THE DETERMINATION OF PHOSPHOTUNGSTATE HUMIN[1].

The precipitate was transferred to a 500 cc. separatory funnel with a spatula and by washing. It was then shaken with 5–10 cc. of concentrated hydrochloric acid and enough of a 1 to 1 amyl alcohol-ether mixture so that it floated on top after all the precipitate had gone into solution. The solution did not become entirely free from turbidity due to the presence of phosphotungstate humin which was removed by passing the entire solution through a Büchner funnel. The nitrogen content of the precipitate was determined by the Kjeldahl-Gunning-Arnold method. The water solution of the bases was then separated from the amyl alcohol-ether mixture and extracted with 3 or 4 successive 50 cc. portions of the mixture and finally the combined amyl alcohol-ether solutions were extracted with about 100 cc. of water to remove any traces of the bases. The wash water was extracted with a fresh portion of amyl alcohol-ether mixture before being added to the main solution of the bases. The solution of the bases was evaporated to dryness in the vacuum distilling apparatus in order to remove the excess hydrochloric acid and then it was taken up with hot water, transferred to a 50 cc. graduated flask, cooled and made up to the mark.

ARGININE.

Arginine was determined on a 25 cc. aliquot of the solution of the bases using Plimmer's[3] modification and an apparatus as modified by Koehler[4]. Twenty-five cc. of 40% sodium hydroxide were added to the aliquot in a 200 cc. Kjeldahl flask. The flask was attached to a reflux condenser the upper end of which was connected by a glass tube to a bottle containing 15 cc. of N/14 hydrochloric acid. Air was drawn through the apparatus during the 6 hours' boiling, after which the water was drawn

---

[1] Gortner R. A., and Holm, G. E., *J. Am. Chem. Soc.*, 1917, **39**: 2477.
[2] *Z. physiol. Chem.*, 1901, **34**: 153.
[3] *Biochem. J.*, 1916, **10**: 115.
[4] *J. Biol. Chem.*, 1920, **42**: 267.

from the condenser and the boiling continued for about 20 minutes in order to drive off all the ammonia. The excess acid was titrated with N/14 ammonia, using methyl red as an indicator.

TOTAL NITROGEN OF THE BASES.

The solution remaining after the arginine determination was completed was transferred to a 500 cc. Kjeldahl flask and nitrogen determined by the Kjeldahl-Gunning-Arnold method. The nitrogen driven off as ammonia during the arginine determination added to this gave the total nitrogen of the bases.

CYSTINE.

Cystine was determined by Denis's[1] modification of Benedict's[2] method. An aliquot of 10 cc. of the solution of the bases was transferred to a 10 cm. evaporating dish and 5 cc. of a solution containing 25 grams of copper nitrate, 25 grams of sodium chloride, and 10 grams of ammonium nitrate per 100 cc. of water were added. It was then evaporated to dryness on the water bath and gradually heated to a dull red heat which was maintained for about 10 minutes. The black residue was dissolved in 10 cc. of 10% hydrochloric acid, diluted to 150 cc., and heated to boiling. To the boiling solution 10 cc. of 5% barium chloride were added slowly and with stirring. The precipitate was allowed to digest overnight on a steam bath after which it was filtered hot through a No. 589 S. & S. blue-ribbon filter paper. It was then washed till free from chlorides with hot water, ignited at a dull red heat and weighed. A blank was run on the reagents and the necessary correction made.

AMINO NITROGEN OF THE BASES.

Amino nitrogen was determined by the Van Slyke[3] method of decomposing the amino acid with nitrous acid in the micro apparatus[4]. Two cc. of the solution of the bases were allowed to react for 30 minutes in the micro apparatus after which the amount of nitrogen evolved was read, the temperature and pressure being noted.

HISTIDINE (Calculated)[5].

Histidine was determined by solving the formula,

$$\text{Histidine N} = 3/2\ (\text{D} - \tfrac{3}{4}\ \text{arginine})$$
$$= 1.5\ \text{D} - 1.125\ \text{arginine},$$

D being the difference between the total nitrogen of the bases and the amino nitrogen determinations, or the nonamino nitrogen.

LYSINE (Calculated).

Lysine nitrogen was determined by difference.

$$\text{Lysine N} = \text{Total N of the bases} - (\text{Arginine N} + \text{Cystine N} + \text{Histidine N}).$$

TOTAL NITROGEN OF THE MONOAMINO ACIDS.

The combined filtrate and washings of the phosphotungstate precipitate were rendered just alkaline by adding 50% sodium hydroxide and then just cleared of the turbidity formed by adding 50% acetic acid. The acid solution was concentrated in vacuo until salt began to crystallize out when the solution was transferred to a 250 cc. graduated flask and made up to the mark. The total nitrogen was

---

[1] *J. Biol. Chem.*, 1910, **8**, 401.
[2] *Ibid.*, 1908, **6**, 363.
[3] *Ibid.*, 1911, **9**, 185; 1912, **12**, 275.
[4] *J. Biol. Chem.*, 1913, **16**, 121; 1915, **23**: 407.
[5] *Ibid.*, 411.

determined on a 50 cc. aliquot by the Kjeldahl-Gunning-Arnold method; the digestion, however, was continued for 3 hours after the solution had become clear in order that the phosphotungstic acid present would not interfere with the determination.

AMINO NITROGEN OF THE MONOAMINO ACIDS.

A 4 cc. portion of the solution was allowed to react with the nitrous acid for 6 minutes in the micro apparatus after which the volume of nitrogen evolved was read and the temperature and pressure noted.

NONAMINO NITROGEN (Calculated).

The nonamino nitrogen of the monoamino acids was determined by difference.

Nonamino N = Total N − Amino N.

TOTAL SULFUR[1].

Inasmuch as sulfur is lost during the hydrolysis of proteins it was decided to determine the total sulfur content on the original sample in order that a comparison might be made with the percentage of sulfur found in the cystine determination.

Ten grams of sodium peroxide were placed in a 100 cc. nickel crucible and enough water added so that it was completely decomposed to sodium hydroxide. The solution was heated over an alcohol flame until a scum formed on the surface of the liquid on cooling. One gram of protein was added and thoroughly mixed with the sodium hydroxide with a nickel stirring rod. The heating was continued until the mass in the crucible subsided and changed from a brown to a black oily appearing liquid.

After a few minutes of heating small amounts of sodium peroxide were added till the oxidation was complete. The substance was cooled, dissolved in water, transferred to a 600 cc. beaker and strongly acidified. It was then boiled to drive off the excess chlorine, exactly neutralized with ammonium hydroxide, 4 cc. of concentrated hydrochloric acid added and evaporated to a volume of 400 cc. if necessary. Ten cc. of hot 10% barium chloride were added slowly and the solutions allowed to stand overnight on a steam bath. Then they were filtered hot through No. 589 S. & S. blue-ribbon filters, washed with a little weak hydrochloric acid solution and then with hot water till free from chlorides. They were ignited, weighed and calculated as percentage of sulfur and as percentage of nitrogen as cystine, assuming all the sulfur was present as cystine.

TOTAL NITROGEN.

One gram of the original sample was weighed out and placed in a Kjeldahl flask and digested. The solution was made up to volume and a fifth aliquot taken for distillation. All operations were carried out as in the Kjeldahl-Gunning-Arnold method. It was necessary to know the total nitrogen of the original sample, since the sulfur was determined directly, in order to make the percentage of nitrogen as cystine comparable with the figures of the Van Slyke analysis.

The results of the analyses are shown in the table, where the nitrogen in each fraction is expressed in percentage of the total nitrogen. The nitrogen in the air-dry material varied from 12.50 to 13.61 per cent. The sample was fat free but not moisture and ash free. The moisture and ash were not determined and consequently it is necessary to present the results as indicated.

---

[1] Osborne, T. B., *J. Am. Chem. Soc.*, 1902, **24**: 140.

Nitrogen distribution of globulin-albumin fraction of lean beef round.

(Percentage of total nitrogen.)

CONSTITUENT	SAMPLE NO.		
	504	592	594
Ammonia nitrogen	6.18	6.93	6.98
Acid insoluble humin nitrogen	1.14	0.82	0.55
Acid soluble humin nitrogen	1.98	1.75	1.68
Phosphotungstate humin nitrogen	0.69	0.80	0.73
Arginine nitrogen	14.64	12.98	14.10
Cystine nitrogen	1.40	0.80	1.01
Lysine nitrogen	14.92	11.96	14.96
Histidine nitrogen	2.76	10.32	3.82
Total nitrogen of the bases	33.71	36.05	33.88
Amino nitrogen of the monoamino acids	55.34	55.99	58.64
Nonamino nitrogen of the monoamino acids	2.88	2.61	2.59
Total nitrogen of the monoamino acids	58.22	58.60	61.23
Total recovery	101.92	104.95	105.05
Total nitrogen in air-dry sample	12.50	13.61	13.40

The monoamino acids comprise 58 to 60 per cent of the total nitrogen and the arginine and lysine nitrogen 14 to 15 per cent in a normal animal. The histidine nitrogen runs from 3 to 4 per cent and the cystine nitrogen 1 to 1.5 per cent. The total humin nitrogen runs 3 to 4 per cent. Sample 592 was not from a normal animal and differed in some respects from the other samples. This phase of the matter will be discussed in a future paper.

No report on gelatin was made by the referee.

W. F. Hand.—This morning we congratulated ourselves that we had a scientist in the Senate. We must not forget that we have a scientist as the administrative head of one of the largest government departments. We are very glad that he is a scientist. We believe that he is a better administrative head because he is. I believe Secretary Wallace is somewhat of a chemist. We also believe that is a hopeful sign. We count ourselves distinctly honored that he has consented to come here and make an address, and we will now be very glad to hear him.

ADDRESS BY THE SECRETARY OF AGRICULTURE—THE HONORABLE HENRY C. WALLACE.

As you expect me to be perfectly honest, I must disclaim some of the honor which your chairman has so generously accorded me. I cannot claim to be a scientist of very long standing. You notice I wear your badge, but I did not come by it very honestly. Some very nice young lady pinned it on me out there. A long time ago I was engaged for a time in certain lines of scientific work, but I fear the record I made

would not entitle me to admission to a scientific body of real standing, such as this, and I did not come here with the thought that I could contribute anything worth while to your deliberations, but rather to show in a personal way my interest and the interest of the Department in the work you are doing.

Coming over, I learned from one of the committee for the first time that this lusty young organization is a child of our own Department. It gives the Department a feeling of pride, just as every parent has a feeling of pride when the young man grows up and goes out on his own hook and is able to take care of himself. So I think everyone in the Department has a deep sense of satisfaction in noting the growth made by this association, and the splendid work you have done.

I shall not undertake now to tell the story of the service which the chemist has rendered to agriculture. It is a most interesting story, and in it are some of the most brilliant chapters in scientific history. Permit me to say, however, that the opportunities in the future will call to you just as strongly as they have in the past. We have been going through what we might call the period of agricultural exploitation. We had seemingly unlimited areas of fertile land, simply waiting for our people to go in and possess it. That is what we have been doing up to the last ten or fifteen years—possessing the land and harvesting the fertility of the soil. For the past year agriculture has been in a very severe state of depression; indeed, the most serious we have ever experienced. We are, as it were, smothered in our own sweetness. We seem to have a great surplus of food, more than we can use ourselves under present economic conditions. But this will not continue, and when we wear our way through this period of instability and economic distress, I think we shall find ourselves at the beginning of what will prove to be a new era, so far as our agriculture is concerned. Population has been growing steadily. Our easily cultivated land already has been taken up. We still have arid land which can be brought into production by the addition of water; swamp land which needs draining; and cut-over land which will produce when cleared of the stumps. But the chances are that the needs of our increasing population cannot be met by the addition of new plow lands. These needs must be met by increasing production on land already under the plow. If this is true, and I think it is, then the scientist will be called upon even more urgently than in the past to help the farmer by showing him how to develop higher yielding strains and varieties, how to improve his cultural methods, how to combat plant pests and diseases of one sort or another, how to utilize not only products which heretofore have gone to waste very largely, but how to utilize at a profit surplus crops in times of plenty.

I do not need to emphasize the importance of the chemist in this

program of crop improvement, reduced production cost and greater utilization. Your minds have passed mine already and anticipate what I would say if I were to elaborate the suggestion just made. Our debt to the chemists who have given especial attention to agricultural problems already is very great, more than we can ever repay, but the very fact that they have contributed so generously and so splendidly in the past gives us warrant for expecting more and more of them in the future.

Before I close, permit me to say that during the time I have been in the Department of Agriculture I have been very much impressed with the thoroughly conscientious, unselfish, scrupulously honest work of our chemists who have to do with food control; and not alone those in the Department, but those with whom we cooperate in the various States. You who have to do with this work realize that you occupy a position of very great responsibility, and we who have an opportunity to observe your work know that you are measuring up to this in a very fine way. You stand between the producer and consumer and the unscrupulous manufacturer. You stand also for the utilization of waste while preventing that utilization of waste masquerading under false colors to the harm of products which do not come from waste utilization. Speaking for the Department of Agriculture, I am proud of the fine record our chemists have made. It is an inspiration to everyone who gets an understanding of it.

All I can say further is that, speaking for the Department, our heart interest is with you in the work you are trying to do. We are interested in every improvement you make in methods. We are interested in everything you do toward making even better our control of foods and drugs, in order that the consumer may be assured of wholesome products and the producer's interest may be properly conserved. So I bring to you the very best wishes of everyone connected with our Department, and the pledge in their behalf to hold up your hands and work with you in every possible way in the common cause.

REPORT ON SPICES AND OTHER CONDIMENTS.

By ARTHUR E. PAUL[1] (U. S. Food and Drug Inspection Station, Cincinnati, Ohio), *Associate Referee.*

Many features of the official and tentative methods for the examination of spices and other condiments are not entirely satisfactory. Those for prepared and powdered mustard[2] are perhaps more urgently in need of attention and possibly revision than others. In fact, so necessary seemed this revision that before the collaborative work reported in this

[1] Presented by W. C. Geagley.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 261, 97.

paper was done, R. W. Hilts and R. Hertwig of the U. S. Food and Drug Inspection Station, San Francisco, Calif., had made a study of this problem. Their modification of the present method for the determination of crude fiber in prepared mustard and other available details were submitted for collaborative study.

Some years ago Carl S. Miner, Chicago, Ill., conducting a similar investigation, prepared known mixtures of mustard, the ingredients of which had been previously examined as to fiber content. This investigation resulted in the formulation of a set of details which was also submitted.

In accord with the recommendation of last year's associate referee the present tentative method for the determination of volatile oil in mustard seed[1] was also included in the instructions sent to collaborators, with a view to its adoption as an official method in the event that the results obtained proved to be satisfactory.

One sample each of prepared and powdered mustard was submitted to those association members who volunteered to cooperate on the subject of spices and condiments. They were requested to make the indicated determinations by the methods which were submitted and also to make full comments and suggestions as to additional work or investigations.

DETERMINATION OF CRUDE FIBER IN PREPARED MUSTARD.

Although the tentative method for crude fiber is given a special caption under Prepared Mustard in the Book of Methods, it is not complete, since there is included a reference to a more general description of the crude fiber method under Foods and Feeding Stuffs. By this arrangement there is introduced some uncertainty relative to the details involved in the handling of the finally separated fiber. Therefore the method submitted to collaborators as the tentative method was reconstructed as follows:

Method I.

Transfer 8 grams of the sample (equivalent to about 2 grams of dry matter) to a porcelain or glass mortar. Treat with a little hot dilute sulfuric acid (1.20 grams per 100 cc.) and rub to a uniform thin paste. It is absolutely essential that this paste be uniform in consistency and entirely free from lumps. Rinse the thin mixture into a 500 cc. Erlenmeyer flask using a total volume of 200 cc. of the hot dilute sulfuric acid for the entire operation. Connect the flask with a reflux condenser, the tube of which passes only a short distance beyond the rubber stopper into the flask, or simply cover a tall conical flask, which is well suited for this determination, with a watch glass or short-stemmed funnel; boil at once and continue boiling gently for 30 minutes. A blast of air conducted into the flask will serve to reduce the frothing of the liquid. Filter through linen and wash with boiling water until the washings are no longer acid; rinse the substance back into the flask with 200 cc. of the boiling dilute sodium hydroxide

[1] *Ibid.*, 259.

solution, boil at once and continue boiling gently for 30 minutes as directed above for the treatment with acid, filter at once rapidly and wash with boiling water until the washings are neutral. The last filtration may be performed upon a Gooch crucible, a linen filter or a tared filter paper. If a linen filter is used, rinse the crude fiber, after washing is completed, into a flat-bottomed platinum dish by means of a jet of water; evaporate to dryness on a steam bath, remove all the fat by repeated washings of the dry fiber with ether, again dry first on a steam bath and then to constant weight at 110°C.; weigh, incinerate completely, and weigh again. The loss in weight is considered to be crude fiber. If a tared filter paper is used, weigh in a weighing bottle. In any case the crude fiber after drying to constant weight at 110°C. must be incinerated and the amount of the ash deducted from the original weight.

Method II.

Same as Method I except that the final washing with water is followed by washing with alcohol and then ether.

Method III.

(Proposed by Hilts and Hertwig.)

Weigh 10 grams of the sample and transfer to an 8 ounce nursing bottle with 50 cc. of strong alcohol, stopper and shake vigorously. Add 40 cc. of the ethyl ether, shake and let stand about 5 minutes with occasional shaking. Centrifuge and decant off the alcohol-ether mixture. Treat twice more with 40 cc. portions of ether, shaking, centrifuging and decanting as before. Transfer the extracted material to a 500 cc. Erlenmeyer flask with as small an amount as possible of the 1.25% sulfuric acid, cool, and expel the ether by heating and shaking. Now add a sufficient amount of the boiling hot dilute sulfuric acid to complete the 200 cc. Proceed as directed in VII, 66[1], beginning with the eighth line "connect the flask * * *". If preferred the sample may be treated with the alcohol and ether in a small beaker, finally transferring to a hardened 11 cm. filter paper and washing two or three times with ether. Permit to drain completely, but not to dry or cake, and proceed as above.

Method IV.

(Proposed by Carl S. Miner.)

Transfer 8 grams of the sample (equivalent to 2 grams of dry matter) to a small evaporating dish. Add sufficient acetone to make a thin cream and then, gradually, a total of 50 cc. of acetone. Boil the perfectly homogeneous mixture for a few minutes, allow to settle and decant the clear supernatant acetone through linen and repeat the operation twice, using 40 cc. and 30 cc. of acetone. Allow the dish to stand until most of the acetone has disappeared. Add sufficient 1.25% sulfuric acid to make a smooth, thin cream and transfer completely with a small amount of the acid to a 500 cc. Erlenmeyer flask. Expel the acetone by heating and shaking. Now add sufficient of the boiling hot acid to make a total of 200 cc., washing off any mustard that may be on the linen; connect the flask with a reflux condenser and proceed as directed in VII, 66[1].

COMMENTS BY COLLABORATORS.

J. H. Bornmann.—The tentative A. O. A. C. method appears to be unsatisfactory in that it specifies washing with ether after drying the fiber. It is impossible to wash out the fat after the fiber has been dried.

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 98.

Results of collaborative determinations.

Analyst	Total Solids	Crude Fiber			
		Method I	Method II	Method III	Method IV
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
J. H. Bornmann, U. S. Food and Drug Inspection Station, Chicago, Ill.	15.82 15.80	1.28 1.39	0.98 0.97	0.91 0.90	0.92 0.90
Carl S. Miner.	. . . .	1.33 1.39	1.35 1.41	0.94 0.95	1.25 1.25
W. D. Richardson, Swift & Co., Chicago, Ill.	16.04 . . .	1.43	1.04	0.88	0.88
W. B. Owen, Agricultural Department, Tallahassee, Fla.	16.19 16.26	2.25 2.37	1.57 1.71	1.07 1.06	1.19 1.25
R. Hertwig.	15.92 15.95	1.22 1.27	1.01 1.02	0.99 1.01	1.02 1.02

Method II differs from Method I in that the fiber is washed with alcohol and ether before drying. Fairly good results are obtained by this method, though the results are somewhat higher than those obtained by Methods III and IV. Identical results were obtained by the latter methods. There is some advantage in centrifuging. The solvent may be decanted almost completely, and there is no need of decanting on a filter, since the mustard remains packed in the bottom of the flask.

With regard to cost, the advantage lies with Method III. It is also easier to remove the last trace of ether. When extracting with acetone the mixture must be heated cautiously as there is great danger of violent bumping. Centrifuging requires less time and is more effective than boiling and decanting. The third method appears to be preferable for the reasons just enumerated, though it requires more time and there is more danger of loss of material.

The difference between results obtained by Methods III or IV and Method II is not very great. If Method III were adopted, the existing standard for crude fiber ought to be lowered, in which case the end results would probably be the same; that is, a mustard judged by the present standard for fiber using Method II would appear as good as it would when judged by a lower standard using Method III.

Carl S. Miner.—I prefer to use alundum crucibles instead of Gooch crucibles. About ½ to ¾ of an hour was required for filtration through Gooch crucibles.

In Method IV I believe it would be better to use a beaker instead of an evaporating dish and to boil for longer periods, also to use a larger quantity of solvent, because I am sure I did not remove all the oil by following Method IV as written.

Method III seems to me to be the best method, and it is the easiest to manipulate.

W. D. Richardson.—Method I apparently gives high results. The fiber, after washing with ether, appears waxy and gummy before drying, and with Method II a somewhat similar appearance is produced. In both Methods I and II the material adheres to the linen on the first filtration, perhaps due to the oils and gums present. Methods III and IV, although perhaps requiring a little more time and manipulation, appear to give better results. From the work we did we rather favor Method IV as it filters a little more readily and gives a cleaner appearing fiber.

R. J. Owen.—Suggest that the method for total solids allow the use of electric oven as well as water oven. Methods III and IV are simpler and I believe more accurate

than Methods I and II. We prefer Method II on account of its simplicity and because no special apparatus is required. Why should not carbon tetrachloride be a better solvent than acetone? If there had been more sample we would have tried carbon tetrachloride.

R. Hertwig.—In ordinary practice I use hardened filter paper and a Büchner funnel for the first filtration. For the second filtration I add about 1 gram of asbestos at the completion of the alkali digestion, shake well and immediately filter on asbestos in a Hirsch funnel. After the washing with water and finally with alcohol I transfer the entire mat as a unit to a platinum dish, * * * etc. I should think that a similar procedure might be commendable for the acid filtration also, making both filtrations the same. The simplicity of the filtering, washing and transferal surely should be in its favor.

I had been of the opinion that the efficient crude fiber method for prepared mustard gave high results only because of the possibility that the fat present protected the material somewhat from the action of the acid and alkali. At present I am not so certain that this is the only possible cause. Another possible cause is that some fat in the official method remains included in the crude fiber material, which after drying and hardening is not extracted by the ether and thus gets weighed as crude fiber. I hardly think that the use of paper in Method I and asbestos in Method II would explain the difference in results although very possibly the asbestos allows more efficient washing.

Considering this immediate work and also other experience I have had with Methods I and III, which has been considerable, I should recommend Method III as the most satisfactory and at the same time the most reliable one of the four methods. The official method for prepared mustard stands as an exception to the crude fiber determinations of all other materials, in having the fat present. There always is the possibility that this fat may in certain instances cause high results for the two possible reasons as given above. The fat makes the digestions, the filtrations and the washings more or less unsatisfactory. The fat is the cause of lumping. All these objections are eliminated in Method III, which is neat in technique and preferable to the others.

In Method III, I should recommend a slight change in the procedure. Replace the sentence "Transfer the extracted material to a 500 cc. Erlenmeyer * * * etc." and the two subsequent sentences by the following:

> Rest the bottle on its side for a short time, without heat, to allow the ether largely to evaporate. Transfer the material to a 1000 cc. Erlenmeyer flask, using 200 cc. of boiling hot dilute sulfuric acid and proceed as directed under VII, 66.

In this way the procedure is more satisfactory, one is not troubled with frothing and an extra heating is avoided.

CONCLUSIONS.

A glance at the results reported will show at once that the "personal equation" enters into the determination of crude fiber to a marked degree. Of the five collaborators, two reported results which are in each instance higher than those reported by the others. But it will be observed, especially, that the disparity in the results is greatest in the case of Method I. With this method the highest result reported is 2.37 per cent and the lowest 1.28 per cent, a range of 1.09 per cent. In the case of Method II, a slight modification of the tentative method, the extreme range is 0.74 per cent. It would seem that these variations

are quite extreme. For Methods II and III the ranges are, respectively, 0.19 and 0.37 per cent. It is apparent, therefore, that the "personal equation" is reduced to the minimum in the case of Method III.

Attention should also be directed to the fact that in the case of crude fiber a procedure which gives the lowest results would be the most desirable. The lowest results were reported with Method III. All collaborators reported higher figures by all other methods, with the exception that one collaborator reported identical results by Methods III and IV.

DETERMINATION OF VOLATILE OIL IN MUSTARD SEED.

As previously stated, the method submitted to collaborators for study is that which is now included among the association methods as "tentative" and is described in the Book of Methods[1].

The following results show the percentage of volatile mustard oil found in the submitted sample by each collaborator:

J. H. Bornmann	0.67—0.69
W. D. Richardson	0.68
Carl S. Miner	0.70—0.70
R. Hertwig	0.72—0.73

COMMENTS BY COLLABORATORS.

J. H. Bornmann.—The manipulations necessary to this determination are simple and easy, and the method appears to be satisfactory in its present form.

W. D. Richardson.—It would be advantageous to use 0.05N instead of 0.1N solution as specified in the method.

CONCLUSIONS.

The exact proportion of volatile oil in the sample submitted is not known, but in view of the facts that these three skilled analysts obtained such very satisfactory and concordant results and that their work confirms that previously done by this association it would seem that this method should be made official.

RECOMMENDATIONS.

It is recommended—

(1) That the present tentative method for the determination of volatile oil in mustard seed be made official.

(2) That the method submitted by Hilts and Hertwig for the determination of crude fiber in prepared mustard, including the suggestions of Hertwig, be adopted as tentative and replace the present method, and that same be studied by next year's associate referee with a view to its final adoption as an official method.

(3) That consideration be given to the recommendation of last year's associate referee on spices and other condiments, to study methods for the examination of salad dressings.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 259.

REPORT ON DETERMINATION OF SHELL IN CACAO PRODUCTS.

By B. H. SILBERBERG (Bureau of Chemistry, Washington, D. C.), *Referee.*

Various factors have contributed to the enormous growth of the chocolate industry in this country in the last few years. The familiar cakes of chocolate, known in the trade as "bar goods", met ideally the demand created by the war for a compact, highly nutritive food-confection. The export trade received a decided impetus owing to the lowered production of chocolate in the warring countries of Europe, as well as to the increased demand created by the war. The prohibition of alcoholic beverages is also considered a factor contributing to the greater demand for confectionery of all descriptions. This demand naturally led to an increase in production and keener competition which, in turn, brought about the desire on the part of the trade to produce an article as cheaply as possible. This kind of competition always leads to the temptation to adulterate.

The form of adulteration to be considered in this report is the presence of excessive cocoa shells, due either to inefficient cleaning of the nibs or the addition of "fines". This method of adulteration makes more urgent than ever a satisfactory means of determining the amount of shell in cacao products. W. C. Taber, as Referee on Crude Fiber in Cacao Products, in his report to this association last year[1] presented data which showed clearly that the crude fiber method was not a satisfactory or conclusive means of determining the presence of excessive shell. The crude fiber figure will probably not be low if excessive shell is present, but it may be high when practically no shell is present if the product is made from certain types of beans, the nibs of which are high in fiber. Knapp and McClellan[2] in a paper, "The Estimation of Cacao Shell", conclude that "the only method employed by itself which is capable of giving results of any value is the estimation of the crude fiber", but add that "there is no process which will determine so low a percentage as 5 per cent". Such a process would obviously be of little advantage.

The acknowledged inadequacy of chemical analysis to determine excessive shell turns the analyst to the next alternative, the microscope, although the inclination is to regard quantitative microscopy with more or less suspicion. In the discussion following the paper by Knapp and McClellan the point is brought out that microscopic examination should never be omitted, but the paper states that "no analytical method by itself, or in conjunction with others, will enable the analyst to distinguish between cocoa containing two per cent and cocoa containing five per

[1] *J. Assoc. Official Agr. Chemists*, 1921, 5: 258.
[2] *Analyst*, 1919, 44: 2.

cent of shell". This, however, is thought to have been disproved. In his report for 1920 the referee recommended that further study be made of the microscopic method for the examination of cacao products for shells in order that its limit of accuracy might be determined by those experienced in its use.

The method referred to was developed by analysts in the Bureau of Chemistry, and may be stated as follows:

Method for the Quantitative Determination of Cocoa Shell in Cocoa and Chocolate Products.

Eliminate the fat with gasoline or ether in a centrifuge or on a suction filter. In the case of chocolate, shave the sample off so that the defatting agent will penetrate easily. Wash the sample three or four times. If necessary, remove the sample to a mortar, grind, and then continue the defatting process to completion. If the sample contains sugar remove by washing several times with water in the same way and wash finally with a mixture of ether and alcohol. Dry, powder and mix the sample thoroughly. Weigh accurately 2 mgs. and mount on a glass slide (a ruled slide is very desirable) with just sufficient chloral hydrate (1 to 1) to fill in under a square cover glass. Before applying the cover glass stir and spread the material with the point of a needle in order to get a uniform mount. Warm slightly (do not boil) and let stand until tissues have cleared (preferably about 12 hours).

Examine the entire mount, counting all the stone cell groups present. Compare the result with those previously obtained on standard samples containing a known percentage of cocoa shells. The standards used for comparison should be prepared from defatted material, and all results should be reported on the fat-free basis.

NOTE.—The careful preparation of the standard samples is of immeasurable importance. It is not advisable to use as a basis for standards a commercial cocoa which may be assumed to be practically free from shell. The only accurate method is to start with clean cocoa nibs and shells Grind and thoroughly defat both nibs and shells separately until each passes through a 100-mesh sieve Then weigh and mix nib powder and shell powder in desired proportions, finally sieving each standard through the 100-mesh sieve to insure thorough and uniform mixing.

Care should be taken in making mounts not to use too much chloral hydrate as there should be none protruding around the edges of the cover glass. The stone cell groups are often difficult to recognize, especially when partially obscured by other tissues, and some types of tissues may be easily confused with stone cells if the analyst is not experienced in noting fine histological differences. The only way to avoid these difficulties is by careful study of, and constant familiarity with, the various tissues in cocoa.

It is advisable when counting a sample to make a check by counting a standard. A good plan is to count one slide of the sample, then count the standard to which it seems to be nearest in shell content, and then count at least one more slide of the sample.

Pursuant to the recommendation made in last year's report, your referee prepared five standards, according to the instructions outlined in the method, containing 2, 3, 4, 5 and 8 per cent of shell, respectively. Samples of each were sent to each collaborator, the 2 per cent, 4 per cent and 8 per cent being labeled as to their shell content and the 3 per cent and 5 per cent being used as unknowns and labeled A and B, respec-

tively. A copy of the method was also sent to each collaborator, with the following instructions:

It is requested that in making this report each analyst give the counts—at least two on each sample—obtained on the standards and on the unknowns, as well as his estimation of the amount of shell in each unknown. If the first two counts on a sample do not check fairly well, more should be made.

Many samples of nibs taken from the hoppers of mills were examined by analysts in the Bureau of Chemistry to determine the amount of shell present, and various manufacturers were consulted as to how free from shell they could reasonably be expected to clean their nibs. The information obtained from these two sources led to the conclusions that the better grades of cacao products contain not more than 1 per cent of shell on the basis of the nibs, which would be equivalent to 2 per cent on the fat- and sugar-free basis, and that any product containing more than 2 per cent on the basis of the nibs or 4 per cent on the fat- and sugar-free basis can justly be regarded as containing excessive shell. Since 4 per cent on the fat- and sugar-free basis has been recommended as the limit of tolerance for shell it was considered that by making the two unknowns 3 per cent and 5 per cent, respectively, of shell, the results would indicate how sharply the line might be drawn in enforcing this limit. Furthermore, it is not especially important that the method be as accurate beyond 5 per cent as under this percentage, since anything above that is unquestionably excessive. The results of the collaborators are shown in the following table. The counts given represent the widest extremes reported by each analyst. In many cases more than two counts were made.

Counts obtained by collaborators on shell in cacao products.

	Standards			Unknowns			
Analyst	2%	4%	8%	A (3%)	Estimated	B (5%)	Estimated
					per cent		*per cent*
1	18–20	39	74–77	30–32	3.1	48–52	5
2	10–13	29	68–92	28–31	4	40–43	5
3	30–35	54–60	93–98	53–59	4	72–74	6
4	9–16	25–26	57–60	25–29	4	32–43	5.5
5	27–41	73–76	110–153	42–62	3	83–89	5.2
6	32	66	122	43–44	3	89–92	6
7	5–9	2–9	11–16	4–10	4.2	9–18	7
8	17–23	35–42	65	13–16	1.5	24–26	2
9	17	35	.....	28–29	3.0	42	4.5

Of the nine collaborators reporting, only five (1, 4, 5, 6 and 9) are known to be more or less familiar with microscopic work and to have had some experience in the use of the method. Practically nothing is known with respect to the experience of the other four collaborators, but the results of two (2 and 3) lead to the belief that they are at least fairly

familiar with the use of the microscope. The results of the other two (7 and 8), indicate that they have had little experience in micro-analysis or in the use of this method. It would therefore seem unjust to the method to judge it by their results as the statement has been made repeatedly that the method is not one which can be used by a novice in the work. Considering then the results of the other seven, four reported correctly on A, and the other three reported 4 per cent, which was only 1 per cent high. Using only the whole numbers—as it is believed that the accuracy of the method does not warrant reports being given in decimals—four out of the seven reported correctly on B, two reported 6 per cent, which was only 1 per cent high, and, while the other one reported 4.5 per cent, calculating from his own figures, his results indicate practically 5 per cent, the amount present.

It is evident from the results obtained by the collaborators that the personal factor in making the counts is most important; some analysts seem able to identify stone cell groups where others do not. However, if the analyst's counts are consistent on standards, enabling him to report results as shown in the table, it suffices for practical purposes even though it does not place the method entirely above criticism.

In order to determine whether differences of 1 per cent in shell content could be detected the referee placed portions of each of the five samples used in collaborative work in separate vials, marking each one with the amount of shell present. A co-worker removed these marks and substituted letters, for which he kept the key. These samples were then counted by the referee, and the results were so conclusive that the five samples were listed in their proper order without any difficulty whatever.

In view of the results reported by the collaborators and this experiment, your referee considers that the method is worthy of adoption by this association as a tentative method for the quantitative determination of cacao shell in cacao products and so respectfully recommends.

REPORT ON METHODS FOR EXAMINATION OF CACAO BUTTER.

By WALTER F. BAUGHMAN (Bureau of Chemistry, Washington, D. C.), *Referee.*

At the 1920 meeting of the association the Referee on Methods for Examination of Cacao Butter[1] reported the results of a study he had made on the critical temperature of dissolution determination and the Bloomberg[2] acetone-carbon tetrachloride test for hydrogenated oils, tallow, etc., and recommended that these two methods be submitted to collaborators. This recommendation was approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1921, 5: 263.
[2] *Ibid.*, 1920, 3: 493.

The critical temperature of dissolution is the temperature at which a solution of 5 cc. of a melted neutral fat in 5 cc. of glacial acetic acid becomes turbid on cooling. Practically all potential substitutes for cacao butter with the notable exceptions of hydrogenated oils, tallow and oleostearine have a considerably lower temperature of dissolution than cacao butter, and when mixed with pure cacao butter they lower the temperature of dissolution. Free fatty acids also lower the temperature, and it is necessary to determine the acid value of the fat and make a correction. The temperature of dissolution also varies with the strength of the acetic acid; therefore it is recommended in the description of the method that the acetic acid be standardized against an authentic sample of cacao butter. The purity or sophistication of the sample under examination is then indicated by comparing its critical temperature with that of the authentic cacao butter.

The acetone-carbon tetrachloride test is simply the determination of the solubility of the sample in a mixture of equal parts of carbon tetrachloride and acetone. Five cc. of the melted fat are dissolved in 5 cc. of the carbon tetrachloride mixture and the solution cooled in ice water for 20 or 30 minutes. If hydrogenated oil, tallow, oleostearine, lard or paraffin is present a flocculent precipitate is found which goes into solution again—but slowly—when the mixture is removed from the ice water and allowed to come to room temperature. These are qualitative tests.

The critical temperature of dissolution determination will detect the presence of coconut, palm nut and cottonseed oils or stearines, corn oil, peanut oil, etc., but not hydrogenated oils, tallow or oleostearine, while the acetone-carbon tetrachloride test will detect hydrogenated cottonseed oil, tallow, oleostearine and paraffin but not the other possible adulterants.

The following samples and instructions were sent to ten chemists who had expressed a willingness to collaborate in this work:

(1) Cacao butter adulterated with 5% hydrogenated cottonseed oil.
(2) Cacao butter adulterated with 5% coconut stearine.
(3) Cacao butter adulterated with 15% cottonseed stearine.
(4) Cacao butter adulterated with 20% peanut oil.
(5) Cacao butter adulterated with 5% oleostearine.
(6) Cacao butter adulterated with 5% palm kernel oil stearine.
(7) Pure cacao butter with a high content of free fatty acids.
(8) Cacao butter adulterated with 10% tallow.

A sample of pure cacao butter to be used as a standard was also sent.

INSTRUCTIONS TO COLLABORATORS.

Critical Temperature of Dissolution in Acetic Acid.

APPARATUS.

Insert a thermometer reading to 0.1°C. into a cork that fits a 6″x¾″ test tube. The thermometer should extend far enough into the tube that the bulb will be covered by

10 cc. of liquid. Scratch graduation marks on the test tube at 5 cc. and 10 cc. from the bottom. Place the test tube in a larger tube (4"x1¼"), containing glycerine, and hold firmly in place with a cork having a groove cut in the side to equalize the pressure when heat is applied.

REAGENTS.

(a) *Glacial acetic acid.*—As free from water as possible.
(b) *0.1N potassium hydroxide solution.*

DETERMINATION.

To remove traces of moisture filter a portion of the sample to be examined through a dry filter paper in an oven where a temperature of about 110°C. is maintained. Allow the filtered sample to cool until barely warm and run into the test tube up to the 5 cc. mark. Add the acetic acid, reagent (a) up to the 10 cc. mark. (The portions should be measured as accurately as possible.) Insert the cork holding the thermometer and place the test tube in the glycerine bath. Heat and shake the apparatus frequently until a clear solution of the fat and acetic acid is obtained. Allow the solution to cool with constant shaking without removing from the glycerine bath. Note the temperature at which the first indication of turbidity appears. Make a similar test with the same acetic acid on a sample of pure cacao butter. Since fatty acids lower the turbidity temperature, correction must be made for the acid value of the sample.

CORRECTION FACTOR

If the strength of the acetic acid, reagent (a) is such that the turbidity temperature of the pure cacao butter is 90°C., one unit of acid value will cause a reduction of 1.2° in the critical temperature of dissolution. If the turbidity temperature is 100°C., one unit of acid value will cause a reduction of 1.0°. For other turbidity temperatures the correction is proportional.

CORRECTED CRITICAL TEMPERATURE OF DISSOLUTION

Determine the acid value (mg. of potassium hydroxide required to neutralize the free fatty acids in 1 gram of the sample) of both the sample and the pure cacao butter as directed under XXII, 30[1]. Multiply the acid value by the correction factor and add the result to the observed turbidity temperature. The figure obtained is the true critical temperature of dissolution. If this temperature is lower than that of the pure cacao butter, adulteration with coconut, palm kernel, cottonseed oils or stearines—corn oil, peanut oil or other vegetable oil—is indicated.

Solubility in Acetone-Carbon Tetrachloride.

REAGENT.

A mixture of equal parts of acetone and carbon tetrachloride.

DETERMINATION.

Dissolve 5 cc. of the warm fat, which has been filtered through dry filter paper in an oven at about 110°C. to remove traces of moisture, in 5 cc. of the acetone-carbon tetrachloride reagent in a test tube. Allow the solution to stand in ice water for 20 or 30 minutes. Run a blank on a sample of pure cacao butter at the same time. If hydrogenated oil, tallow, oleostearine or paraffin is present a white flocculent precipitate will soon appear. If the water is cold enough the cacao butter may solidify. If a precipitate is formed remove the sample from the ice water and allow it to remain at room temperature for a time. Solidified cacao butter will soon melt and go into solution,

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 250.

but if the precipitate is due to any of the above-mentioned possible adulterants a much longer time will be required for it to go into solution.

Reports were received from four collaborators only, and the results reported by one of these, who incidentally introduced some modifications of his own, differed so greatly from those anticipated and also from those reported by the others that his entire report was discarded.

Results of collaborative work on cacao butter samples.

Analyst*	Acid Value	Temperature of Dissolution: Found	Temperature of Dissolution: Corrected	Variation from Cacao Butter	Conclusions as to Purity from Temperature of Dissolution	Acetone-Carbon Tetrachloride Test
					Pure cacao butter used as standard.	
		°C.	°C.	°C.		
1	0.94	100.0	100.9	.....	.....	.....
2	0.77	92.9	93.7	.....	.....	.....
3	0.95	92.9	94.0	.....	.....	.....
4	1.05	98.8	100.0	.....	.....	.....
					Sample 1	
1	0.96	100.0	100.9	0.0	Adulteration not shown.	Adulterated.
2	0.91	93.1	94.1	+0.4	Adulteration not shown.	Adulterated.
3	1.09	90.8	92.0	−2.0	Adulterated.	Adulterated.
4	1.03	93.3	94.4	−5.6	Adulterated.	Adulterated.
					Sample 2	
1	2.88	92.2	94.9	−6.0	Adulterated.	Adulteration not shown.
2	4.07	82.6	87.3	−6.4	Adulterated.	Adulteration not shown.
3	4.15	84.2	88.9	−5.1	Adulterated.	Adulteration not shown.
4	4.12	87.6	92.0	−8.0	Adulterated.	Adulteration not shown.
					Sample 3	
1	4.08	92.2	96.1	−4.8	Adulterated.	Adulteration not shown.
2	4.10	75.5	80.2	−13.5	Adulterated.	Adulteration not shown.
3	4.21	82.0	86.8	−7.2	Adulterated.	Adulteration not shown.
4	4.28	81.9	86.4	−13.6	Adulterated.	Adulteration not shown.
					Sample 4	
1	3.00	95.0	98.0	−2.9	Adulterated.	Adulteration not shown.
2	2.90	85.0	88.2	−5.5	Adulterated.	Adulteration not shown.
3	2.89	85.8	89.1	−4.9	Adulterated.	Adulteration not shown.
4	3.06	87.8	91.0	−9.0	Adulterated.	Adulteration not shown.

Results of collaborative work on cacao butter samples—Continued.

Analyst*	Acid Value	Temperature of Dissolution: Found	Temperature of Dissolution: Corrected	Variation from Cacao Butter	Conclusions as to Purity from Temperature of Dissolution	Acetone-Carbon Tetrachloride Test
					Sample 5	
1	0.96	100.0	100.9	0.0	Adulteration not shown.	Adulterated.
2	0.89	93.7	94.9	+1.2	Adulteration not shown.	Adulterated.
3	1.12	88.7	90.0	−4.0	Adulterated.	Adulteration not shown.
4	0.92	83.7	84.7	−15.3	Adulterated.	Adulteration not shown.
					Sample 6	
1	2.95	92.5	95.4	−4.5	Adulterated.	Adulteration not shown.
2	4.06	82.4	87.0	−6.7	Adulterated.	Adulteration not shown.
3	4.21	84.6	89.4	−4.6	Adulterated.	Adulteration not shown.
4	4.14	83.1	87.5	−12.5	Adulterated.	Adulteration not shown.
					Sample 7	
1	4.82	96.5	101.3	+0.4	Adulteration not shown.	Adulteration not shown.
2	4.83	89.2	94.9	+0.9	Adulteration not shown.	Adulteration not shown.
3	5.02	87.0	92.7	−1.3	Adulterated.	Adulteration not shown.
4	4.99	89.2	94.5	−5.5	Adulterated.	Adulteration not shown.
					Sample 8	
1	1.02	99.5	100.5	−0.4	Adulteration not shown.	Adulterated.
2	1.08	88.9	90.2	−3.5	Adulterated.	Adulterated.
3	1.15	89.6	90.9	−3.1	Adulterated.	Adulterated.
4	1.12	96.1	97.3	−2.7	Adulterated.	Adulterated.

*Analysts referred to are—
(1) Walter F. Baughman.
(2) C. S. Brinton, U. S. Food and Drug Inspection Station, Philadelphia, Pa.
(3) Llewelyn Jones, U. S. Food and Drug Inspection Station, Chicago, Ill.
(4) M. L. Offutt, Bureau of Chemistry, Washington, D. C.

DISCUSSION.

The results obtained with the acetone-carbon tetrachloride test are quite satisfactory and with one exception are such as were anticipated. Adulteration was detected in Samples 1, 5 and 8 by all collaborators except one who reported Sample 5 as not showing adulteration by this test.

Adulteration of Samples 2, 3, 4 and 6 was detected by the critical temperature of dissolution determination, but these encouraging results are offset by those of two collaborators who also found evidences of adulteration in Samples 1, 5 and 8, which should have shown no evidences by this test, as well as in Sample 7, pure cacao butter.

Brinton (Analyst No. 2) sent the following comments with his report:

It is unfortunate that the critical temperature of dissolution test is not designated as the "Valenta test"[1] as it is spoken of in the older books on oils and fats. I used this test on butter and oleomargarine very satisfactorily about 25 years ago. Pearmain and Moor[2] spoke highly of this test. The use of a glycerine bath is advisable and much better than a water bath. The acetone-carbon tetrachloride test gives good results on some of the samples, but on others the indications are not as clear cut as desirable, their behavior in some particulars being almost identical with the sample of known purity, and yet in others it is very different. Sample 8 is an instance of this. It is believed to be adulterated because it begins to be flocculent and finally becomes solid long before the pure sample, but on redissolving it behaves very similar to the pure sample.

RECOMMENDATION.

It is recommended that further study be given to these two methods.

REPORT ON COFFEE.

By H. A. Lepper (Bureau of Chemistry, Washington, D. C.), *Referee.*

The Power-Chesnut method[3] for the determination of caffeine in coffee was adopted as an official method (first action) at the 1919 meeting. This method is of wide applicability for the determination of caffeine in vegetable material in general. Because of its applicability it is believed desirable to make a minor change in the wording this year. The authors[4] have found that 20 cc. of 10 per cent sulfuric acid are necessary to hydrolyze the saponins in some kinds of vegetable material and that this quantity of acid in the solutions obtained is without action on caffeine. The latter finding was verified by the referee last year. It is, therefore, recommended that the wording of the method be changed to direct the use of 20 cc. instead of 10 cc. of 10 per cent sulfuric acid for the half-hour boiling of the filtrate from the magnesium treatment and that the method be made official with this minor change.

The referee believes that no further effort should be spent on the determination of caffeine in coffee and sees no necessity for the study of any of the methods for the examination of coffee at present. However, if the association desires to continue the study of coffee, it is recommended that the acids of coffee receive attention.

[1] *J. Soc. Chem. Ind.*, 1884, 3: 643.
[2] Aids to the Analysis of Foods and Drugs, 1895.
[3] *J. Assoc. Official Agr. Chemists*, 1921, 5: 271.
[4] *J. Am. Chem. Soc.*, 1919, 41: 1298.

REPORT ON TEA.

By R. E. Andrew (Agricultural Experiment Station, New Haven, Conn.), *Referee.*

As for several years past, the work this year was confined to the study of methods for the determination of caffeine. Last year the Power-Chesnut method was recommended for adoption as an official method for the determination of caffeine in tea, and the second reading of the recommendation of the Stahlschmidt method was withheld pending further study of the method proposed by Bailey and Andrew with a view to the adoption of one or the other of the last-named methods as an optional official method. The data presented last year were obtained chiefly in the laboratory of the Experiment Station in New Haven where the proposed method was devised. The data this year were obtained chiefly from outside collaboration.

COLLABORATION.

Samples were sent to ten chemists who expressed their willingness to cooperate. Reports were received from H. A. Lepper, Bureau of Chemistry, Washington, D. C.; W. S. Hubbard who reported analyses by C. A. Herrmann, U. S. Food and Drug Inspection Station, New York, N. Y.; I. K. Phelps, Bureau of Chemistry, Washington, D. C., who reported analyses by Dorothy B. Scott, Lillian Offutt and J. I. Palmore, and L. E. Walter, Laramie, Wyo., who reported results obtained by H. R. Baker, assistant state chemist.

INSTRUCTIONS TO COLLABORATORS.

Three samples were used, viz., (I) green tea, (II) black tea, (III) mixture of green and black tea. Each sample was finely ground and well mixed. Sub-samples were sent to each collaborator with the following instructions:

Determine caffeine in each of the samples by the modified Stahlschmidt method, the Power-Chesnut method and the proposed method (Bailey-Andrew). The modified Stahlschmidt method follows:

Modified Stahlschmidt Method.

Weigh 3.125 grams of the finely powdered sample into a 500 cc. flask, add 225 cc. of water (this volume will be reduced to about 200 cc. by boiling) attach a reflux condenser and boil for 2 hours. Add 2 grams of dry basic lead acetate and boil for 10 minutes. Cool, transfer to a 250 cc. graduated flask, fill to the mark, filter through a dry filter, measure 200 cc. of the filtrate into a 250 cc. graduated flask and pass hydrogen sulfide through it to remove the excess of lead. Make the solution up to the mark and filter through a dry filter. Measure 200 cc. of this filtrate into an evaporating dish and concentrate to about 40 cc. Wash the concentrated solution with as little water as possible into a small separatory funnel and shake out six times with chloro-

form, using 25, 20, 15, 10, 10 and 10 cc., respectively, combining the several extracts in a second separatory funnel. Treat the combined extracts with 5 cc. of 1% potassium hydroxide, allow the liquids to separate and draw off the chloroform. Wash the aqueous solution in the separatory with chloroform in two portions of 10 cc. each, adding these washings to the main extract. Distil off most of the solvent, transfer to a small tared flask, evaporate, dry at 100°C. and weigh. Test the purity of the residue by determining nitrogen therein and calculate caffeine by the factor 3.464.

The Power-Chesnut[1] and the proposed[2] methods have been published in the proceedings.

NOTES ON METHODS.

Results for caffeine *by weight* and *from nitrogen* are desired.

In the Power-Chesnut method extraction should be continued until the extract is colorless. The heavy magnesium oxide used should meet the U. S. Pharmacopœia requirements.

Evaporation of the last portion of solvent from the caffeine should be done carefully to prevent loss by spattering.

If the results by all the methods outlined can not be obtained those by the modified Stahlschmidt and proposed methods are particularly desired.

RESULTS OF COLLABORATIVE WORK.

The results obtained by the various collaborators are given in Table 1.

COMMENTS OF ANALYSTS.

H. A. Lepper.—As far as the analytical results go there seems to be little to say regarding the methods. The Stahlschmidt method gave me some trouble with emulsion formation during the chloroform extraction, a condition which was entirely absent in the other two methods. It seems to me that the Bailey-Andrew method is less time-consuming than the Stahlschmidt. I do not like the use of the graduated flask for boiling as it might tend to affect the volumetric contents of the flask after it becomes cool.

Dorothy B. Scott.—The largest amount of caffeine and the best checks were obtained from the Bailey-Andrew method.

Lillian Offutt.—The apparatus used for the Power-Chesnut method was a modified Knorr apparatus and extraction was continued for ten hours. I am familiar with the Power-Chesnut method, but not with the other two. The Power-Chesnut method appears to me to be the most accurate method but requires more time than is always convenient for analysis. The Bailey-Andrew method requires less time than the Power-Chesnut and is less subject to error in manipulation, in my opinion, than either the Stahlschmidt (modified) or Power-Chesnut methods.

J. I. Palmore.—In point of time and ease of manipulation the Power-Chesnut method proves superior to the modified Stahlschmidt method. The Bailey-Andrew method is shorter and easier to manipulate than the Power-Chesnut method. A very little, if any, difference was observed in the appearance of any of the residues from the alcohol and chloroform extractions. The average of duplicate results of the three methods agrees within the limits of experimental error. There is practically no difference in the results obtained by the Kjeldahl and the Kjeldahl-Gunning-Arnold method for nitrogen in the extracted matter. In the Power-Chesnut method, the Rask extractor proved superior to the Soxhlet extractor.

---

[1] *J. Assoc. Official Agr. Chemists*, 1921, 5: 290.
[2] *Ibid.*, 292.

Table 1.

Caffeine in tea.

Analyst	Modified Stahlschmidt Method				Power-Chesnut Method				Bailey-Andrew Method			
	By Weight		From Nitrogen		By Weight		From Nitrogen		By Weight		From Nitrogen	
	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
H. A. Lepper	1.97	2.28	1.97	2.16	2.09	2.15	1.98	2.06	2.10	2.29	1.92	2.10
	....	....	....	...	2.05	2.24	1.99	2.17	2.11	2.31	1.92	2.16
Dorothy B. Scott	2.30	2.17	1.60	1.65	2.09	2.49	1.93	2.32	2.38	2.35	2.05	2.14
	2.02	2.03	1.65	1.75	1.85*	..*	1.79	...	2.14	2.19	1.96	2.15
Lillian Offutt	2.10	2.16	1.63	1.75	2.36	2.55	2.09	...	2.08	..	1.65	....
	2.00	2.10	1.55	1.58	2.34†	2.37†	2.15	2.21	2.00	2.20	1.85	2.13
J. I. Palmore	2.33	2.56	1.94	1.99	2.15	2.32	.	2.20	2.20	2.37	2.02	2.22
	2.19	2.39	1.81	2.02	2.16‡	2.33‡	...	2.21	2.29	2.28	2.02	2.12
	....	....	....	..	...	2.38	..	2.21	..	2.22	...	2.05
	....	...	...	..		2.35*	.	2.20	...	2.50	..	2.23
H. R. Baker	2.63	2.28	1.73	1.78	..	.			1.96	2.36	1.63	1.97
	2.32	2.29	1.73	1.68	.	...	..	..	2.15	2.39	1.68	...
	2.17	2.28	1.82	1.92	..	..	.	..	2.33	2.40	1.73	1.97
R. E. Andrew	2.18	2.28	2.08	2.25	2.33	2.52	2.25	2.42	2.20	2.38	2.16	..
	2.19	2.29	2.08	2.22	2.34	2.46	2.26	2.37	2.25	2.40	2.17	2.30
	....	....	....	...	..	....	..	....	2.20	2.39	2.15	2.33
	...	....	...	.	..	...	....	...	2.20	2.40	2.15	2.33
C. A. Herrmann	2.23	..	2.25	...		..		..	2.34	..	2.25	....

Sample III.

	Modified Stahlschmidt: By Weight	Modified Stahlschmidt: From Nitrogen	Power-Chesnut: By Weight	Power-Chesnut: From Nitrogen	Bailey-Andrew: By Weight	Bailey-Andrew: From Nitrogen
R. E. Andrew	2.43	2.37	2.49	2.44	2.53	2.51
	2.43	2.39	2.39	2.32	2.53	2.52
C. A. Herrmann	2.45	2.42		.	2.56	2.54

*Rask extractor used.
†Modified Knorr extractor used.
‡Soxhlet extractor used.

H. R. Baker.—I consider the Bailey-Andrew method to be better than the modified Stahlschmidt owing to the difficulty in the entire removal of lead by the hydrogen sulfide. Also better checks were obtained from the Bailey-Andrew method.

DISCUSSION OF RESULTS.

The experience with these three methods was summarized by the referee last year as follows:

The results obtained by the proposed method[1] are in close agreement with those obtained by the other two methods and the caffeine residues are of an equal degree of purity. The time required is very much less than in either of the other procedures. (The average difference between results for caffeine by weight and from nitrogen was considerably under 0.10% and practically the same in all methods.)

The results this year show satisfactory agreement as regards results for caffeine by weight but too wide discrepancies between these figures and the corresponding results estimated from nitrogen. The trouble quite evidently lies in the determination of caffeine nitrogen, but why this should be at all troublesome, or why it should be more so in the case of the Stahlschmidt method than in the other methods, is difficult to understand. An allowance of 0.1 per cent for experimental error in determining nitrogen (equivalent to 0.35 per cent caffeine) is a very liberal tolerance and about twice as great as is generally necessary; nevertheless, excluding only those figures for caffeine from nitrogen which vary from caffeine by weight by more than 0.35 per cent the averages for the three samples become as follows:

TABLE 2.

Summary of results on determination of caffeine.

Sample No.	Modified Stahlschmidt Method		Power-Chesnut Method		Bailey-Andrew Method	
	By Weight	From Nitrogen	By Weight	From Nitrogen	By Weight	From Nitrogen
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
I	2.20	2.04	2.18	2.06	2.18	2.02
II	2.26	2.10	2.38	2.24	2.34	2.19
III	2.44	2.39	2.44	2.38	2.54	2.53

In computing this summary all the figures reported by the Power-Chesnut method were included. Of the results reported by the Bailey-Andrew procedure only five were excluded. It was necessary to exclude 16 of the 28 results reported by collaborators by the Stahlschmidt method, as it is manifestly unfair in this case to recognize results which vary from the results by weight to the extent of from 0.5 to nearly 1 per cent, since it is evident that the results by weight are in satis-

[1] Bailey-Andrew Method.

factory accord with the other two methods, and there are ample data to show that the method will yield caffeine residues of equal purity. The summary given is reasonably fair to all methods although it will be noted that the Power-Chesnut method gains by the fact that reports are less complete by that method than by the other two. If all figures reported had been included in the averages in the summary the only conspicuous change would occur in the results for caffeine from nitrogen in Samples I and II by the Stahlschmidt method.

The accumulated data of the past two years show that the Bailey-Andrew method compares satisfactorily with the other two methods, both as regards the gross amount of caffeine obtained and the degree of purity of the caffeine residues. In the opinion of all collaborators it is simpler to manipulate and requires less time than the Stahlschmidt method and, in the opinion of some, it is superior to the Power-Chesnut method in this respect. Your referee, however, feels justified in repeating the recommendation of last year with regard to the Power-Chesnut method and in offering the Bailey-Andrew method as an optional official method.

RECOMMENDATIONS.

It is therefore recommended—

(1) That the Power-Chesnut method as described on page 290 of Volume V of *The Journal* (except that in line 8, 10 cc. of 10 per cent sulfuric acid be changed to read 20 cc. of 10 per cent sulfuric acid) be adopted as an official method for the determination of caffeine in tea. (Second reading.)

(2) That the Bailey-Andrew method be adopted as an optional official method for the same determination. (First reading.)

(3) That suggestions for further study of the subject of tea be left to the next referee.

No report on nitrogen in foods was made by the referee.

The meeting adjourned at 5 p. m. for the day.

THIRD DAY.

WEDNESDAY—MORNING SESSION.

REPORT OF THE COMMITTEE ON EDITING METHODS OF ANALYSIS[1].

The work of your Committee on Editing Methods of Analysis during the past year has been practically confined to the compilation of the additions and changes which were made to the several chapters of the methods at the 1920 meeting, which compilation is given as a part of this report.

Your committee expects during the coming year to consider plans for the next revision of the Book of Methods, and takes this opportunity of requesting suggestions from the members of the association for ways and means of improving and making more useful and convenient the book itself, the arrangement of the chapters, the descriptive matter, cross references, etc. It is urged that all chemists and others who have occasion to use these methods submit to any of the members of the Committee on Editing Methods of Analysis such criticisms as they may have of the present book, together with suggestions that occur to them for improvement in the next edition. These will be gratefully received by your committee and given careful consideration in formulating plans for the next revision.

CHANGES AND ADDITIONS TO THE OFFICIAL AND TENTATIVE METHODS OF ANALYSIS MADE AT THE 1920 MEETING OF THE ASSOCIATION.

I. FERTILIZERS.

The Ross-Deemer method for the determination of boric acid in fertilizer materials and mixed fertilizers was adopted as a tentative method. (First action by the association.) The method has been published in *The Journal*[2].

II. INORGANIC PLANT CONSTITUENTS.

No additions or changes were made at the 1920 meeting.

III. WATERS.

No changes or additions were made to the methods for waters at the 1920 meeting. The association, however, approved a recommendation

[1] Presented by R. E. Doolittle.
[2] *J. Assoc. Official Agr. Chemists*, 1922, 5: 327.

made by Subcommittee A that the following statement relative to the determination of bromide in the presence of chloride and iodide be published in the proceedings for the information of chemists having occasion to make the determination pending the final adoption of a method:

A volumetric method for the determination of bromide in the presence of chloride and iodide will be found in the J. Ind. Eng. Chem., 1920, 4: 358. Cooperative work indicates that this is probably the best method for bromide which has been published, but the results obtained show that only about 95% of the bromide present is recovered when 80 milligrams of bromide are contained in the portion of sample used for analysis. The method is satisfactory in the absence of iodide as shown by the cooperative work on water in 1919[1].

IV. TANNING MATERIALS.

No additions or changes were made at the 1920 meeting.

V. LEATHERS.

No additions or changes were made at the 1920 meeting.

VI. INSECTICIDES AND FUNGICIDES.

The hot bromate method[2] for the titration of the acid distillate in the official distillation method for the determination of total arsenic in Paris green was adopted as an official method. (First action by the association.)

The bromate method[2] for the determination of arsenious oxide in Paris green was adopted as an official method. (First action by the association.)

The bromate method[3] for the determination of arsenious oxide in calcium arsenate was adopted as an official method. (First action by the association.)

The official distillation method[4] for the determination of total arsenic in Paris green was adopted as an official method for the determination of total arsenic in London purple. (First action by the association.)

The zinc oxide-sodium carbonate method[5] for the determination of total arsenic in London purple was adopted as an official method. (First action by the association.)

The bromate method[5] for the determination of arsenious oxide in zinc arsenite was adopted as an official method. (First action by the association.)

The official method[6] for the determination of water-soluble arsenic in lead arsenate was adopted as an official method for the determination of

[1] *J. Assoc. Official Agr. Chemists*, 1921, 4: 381.
[2] *Ibid.*, 5: 34.
[3] *Ibid.*, 36.
[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 54.
[5] *J. Assoc. Official Agr. Chemists*, 1921, 4: 397.
[6] *Assoc. Official Agr. Chemists, Methods*, 1920, 59.

water-soluble arsenic in zinc arsenite. (First action by the association.)

The tentative method[1] for the determination of arsenious oxide in lead arsenate was adopted as a tentative method for the determination of arsenious oxide in calcium arsenate.

The following method[2] for the determination of calcium oxide in calcium arsenate was adopted as a tentative method:

Dissolve 2.0 grams of the sample in 80 cc. of acetic acid (1 to 3), transfer to a 200 cc. volumetric flask and make to volume. Filter through a dry filter and transfer a 50 cc. aliquot to a beaker: dilute to 200 cc., heat to boiling and precipitate the calcium with ammonium oxalate. Allow the beaker to stand 3 hours on the steam bath, filter and wash with hot water. Dissolve the precipitate in dilute sulfuric acid and titrate with permanganate.

A modified method[3] for the determination of calcium oxide in calcium arsenate was adopted as a tentative method.

Under the heading "General procedure for the analysis of a product containing arsenic, antimony, lead, copper, zinc, iron, calcium, magnesium, etc.", applicable to such preparations as Bordeaux-lead arsenate, Bordeaux-zinc arsenite, Bordeaux-Paris green, Bordeaux-calcium arsenate, methods[4] for the determination of lead oxide and copper were adopted as official methods (first action by the association) and a method[4] for the determination of zinc oxide was adopted as a tentative method.

The mercury-thiocyanate method[5] for the determination of zinc oxide in zinc arsenite was adopted as a tentative method.

The official method[6] for the determination of water-soluble arsenic in lead arsenate was adopted under suspension of the rules as an official method for the determination of water-soluble arsenic in zinc arsenate. (Final action.)

The official distillation method[7] for the determination of total arsenic in Paris green was adopted under suspension of the rules as an official method for the determination of total arsenic in magnesium arsenate. (Final action.)

VII. FOODS AND FEEDING STUFFS.

No additions or changes were made at the 1920 meeting.

VIII. SACCHARINE PRODUCTS.

No additions or changes were made at the 1920 meeting.

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 59.
[2] *J. Assoc. Official Agr. Chemists*, 1921, **5**: 37, 50.
[3] *Ibid.*, 41.
[4] *Ibid.*, 42, 43.
[5] *J. Assoc. Official Agr. Chemists*, 1921, **5**: 47.
[6] *Assoc. Official Agr. Chemists, Methods*, 1920, 59.
[7] *Ibid.*, 54.

IX. FOOD PRESERVATIVES.

No additions or changes were made at the 1920 meeting.

X. COLORING MATTERS IN FOODS.

The methods for the examination of commercial coal-tar food colors published previously in the proceedings[1], were adopted as tentative methods by the association. (First action by the association.)

XI. METALS IN FOODS.

No additions or changes were made at the 1920 meeting.

XII. FRUITS AND FRUIT PRODUCTS.

No additions or changes were made at the 1920 meeting.

XIII. CANNED VEGETABLES.

No additions or changes were made at the 1920 meeting.

XIV. CEREAL FOODS.

No additions or changes were made at the 1920 meeting.

XV. WINES.

No additions or changes were made at the 1920 meeting.

XVI. DISTILLED LIQUORS.

No additions or changes were made at the 1920 meeting.

XVII. BEERS.

No additions or changes were made at the 1920 meeting.

XVIII. VINEGARS.

No additions or changes were made at the 1920 meeting.

XIX. FLAVORING EXTRACTS.

No additions or changes were made at the 1920 meeting.

XX. MEAT AND MEAT PRODUCTS.

The methods for the examination of gelatin, as published previously in *The Journal*[2], were adopted as tentative methods. (First action by the association.)

XXI. DAIRY PRODUCTS.

No additions or changes were made at the 1920 meeting.

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 198.
[2] *Ibid.*, 343.

XXII. FATS AND OILS.

The Wijs method (XXII, 16[1]) for the determination of iodine absorption number was made an official method. (First action as official method by the association.)

XXIII. SPICES AND OTHER CONDIMENTS.

No additions or changes were made at the 1920 meeting.

XXIV. CACAO PRODUCTS.

No additions or changes were made at the 1920 meeting.

XXV. COFFEES.

The modified Stahlschmidt method (XXV, 15[2]) for the determination of caffeine in coffees was dropped.

The Power-Chesnut method for the determination of caffeine in coffees was adopted as an official method. (First action by the association.) The method has been published in *The Journal*[3].

The Fendler-Stüber method[4] for the determination of caffeine in coffees as modified at the 1919 meeting was adopted as a tentative method. (Second action by the association.)

XXVI. TEAS.

The Power-Chesnut method[5] for the determination of caffeine in teas was adopted as an official method. (First action by the association.) The details of the method are the same as for the determination of caffeine in coffees.

The modified Stahlschmidt method as further modified at the 1919 meeting to provide for the drying of the caffeine residue at 100°C. instead of 75°C. was adopted as an official method. (First action by the association.)

XXVII. BAKING POWDER AND BAKING CHEMICALS.

No additions or changes were made at the 1920 meeting.

EGG AND EGG PRODUCTS.

The following method for the determination of zinc in dried egg products was adopted as a tentative method (first action by the association):

Place 25 grams of the well-mixed sample in an 800 cc. Kjeldahl flask. Add 5 grams of zinc-free potassium sulfate, 3 or 4 glass beads to prevent bumping, 30 cc. of con-

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 245.
[2] *Ibid.*, 270.
[3] *J. Assoc. Official Agr. Chemists*, 1922, 5: 271.
[4] *Ibid.*, 1921, 4: 533.
[5] *Ibid.*, 1922, 5: 290.

centrated sulfuric acid in the case of yolks or whole eggs (25 cc. of the acid in the case of albumens) and 30 cc. of concentrated nitric acid. Do not heat. When spontaneous action subsides, add 10 cc. of concentrated nitric acid. After 2 or 3 additions of concentrated nitric acid the action becomes less violent. Heat gently, at first, continuing the addition of concentrated nitric acid and increasing the temperature as the digestion proceeds until the contents of the flask are straw colored or colorless, after nitric acid fumes have been boiled off. This digestion may be accomplished in the case of albumen in 40 minutes and in the case of yolks or whole eggs in an hour. To the warm digestion flask add 100 cc. of water and pour contents into a 400 cc. beaker, rinsing the flask with two successive 50 cc. portions of water. To the combined water solution add concentrated ammonium hydroxide until faintly alkaline. Pass hydrogen sulfide gas through the solution for 15 minutes which should be sufficient to saturate. (At this point the majority of albumens indicate the presence or absence of zinc. In the case of albumen, if zinc is present, add a diluted solution of ferric chloride containing 0.5 gram of solid ferric chloride. This assists in retaining the zinc sulfide on the paper when filtering. Pass hydrogen sulfide gas through the solution for 15 minutes.) Heat the beaker on the steam bath for 30 minutes. Remove, allow to settle 5–10 minutes and decant through a 9 cm. filter paper, allowing as much of the precipitate as possible to drain thoroughly. Dissolve the zinc sulfide from this precipitate with 10% of hydrochloric acid, the solution after passing through the filter paper being returned to the original beaker. Copper and lead sulfides are insoluble at this point and may be determined by the usual methods. To the hydrochloric acid solution add 5 grams of ammonium chloride and an excess of bromine water and a slight excess of concentrated ammonium hydroxide. Neutralize carefully with 10% hydrochloric acid adding 2 cc. in excess; add 10 cc. of 50% by weight of ammonium acetate and 8–10 drops of 10% ferric chloride solution, or enough to give a distinct reddish tinge. Dilute to about 300 cc. with water and boil for 1 minute. Allow to settle, filter hot and wash with hot 5% ammonium acetate. Pass hydrogen sulfide gas through the filtrate for 15 minutes. Heat for 30 minutes on a steam bath and filter through a weighed heavily padded Gooch crucible, using gentle suction. Wash with hot 5% ammonium acetate solution. Dry in oven and ignite, roasting first. Increased weight of Gooch is due to oxide of zinc. This multiplied by 0.8034 gives the zinc present in 25 grams of sample.

XXVIII. DRUGS.

The following method for the evaluation of hexamethylenetetramine tablets was adopted as a tentative method. (First action by the association.)

REAGENTS.

(a) *Modified Nessler's reagent.*—(1) Dissolve 10 grams of mercuric chloride, 30 grams of potassium iodide and 5 grams of acacia in a minimum quantity of water and filter through a pledget of cotton wool. (2) Prepare a solution of 15 grams of sodium hydroxide in 100 cc. of water.

(b) *Standard iodine solution.*—Prepare a 0.1N solution by dissolving 12.692 grams of purified iodine in a solution of 18 grams of potassium iodide in 300 cc. of distilled water. Dilute the solution to 1000 cc.

(c) *Standard sodium thiosulfate solution.*—A 0.05N solution.

PRELIMINARY TREATMENT.

Ascertain the weight of 20 or more tablets, triturate in a mortar to a fine powder and keep in a small capsule tightly closed with a cork or glass stopper. Weigh out

0.5 gram of the powdered sample on a metal scoop or watch glass, transfer with sufficient water to a round-bottom flask, and add additional water to a total volume of 100 cc. and finally 25 cc. of 10% hydrochloric acid. Connect with a reflux condenser (preferably of the worm type) and boil gently 15 minutes; after cooling, wash out the condenser tube with a little water and transfer the contents of the flask to a graduated 250 cc. flask, finally diluting to the mark with water.

DETERMINATION.

With a pipet withdraw 10 cc. (containing in the case of the pure product the elements of 0.02 gram of hexamethylenetetramine) of the solution so prepared to a 200 cc. Erlenmeyer flask containing a mixture (previously chilled in ice water if available) of 20 cc. of the modified Nessler's reagent solution (1) and 10 cc. of the solution (2), wash down neck of container with a fine jet of water and allow the mixture to stand at least 1 minute after gentle rotation of the flask. Now add 10 cc. of 40% acetic acid in such manner that the inside of the neck is completely washed by the reagent, mix quickly and thoroughly by gently rotating and tilting the flask, and immediately run in from a buret 20 cc. of the standard iodine solution; titrate with the standard sodium thiosulfate solution (adding 5-10 drops of starch solution toward the end of the operation) to the disappearance of the blue coloration. The final color of the solution is a pale straw-green. If preferred, the end-point may be determined by the reformation of a faint blue coloration, induced by the addition of a drop of iodine solution.

Since the standard iodine solution employed has twice the titrimetric strength of the standard thiosulfate and 1 cc. of 0.1N iodine is equivalent to 0.001167 gram of hexamethylenetetramine (0 = 16), the quantity of this product, as represented by its elements formaldehyde and ammonia in the aliquot under examination, may be readily calculated from the expression—

$$\frac{H-I}{2} N \times 0.001167,$$

in which H = the number of cc. of 0.05N sodium thiosulfate equivalent to 20 cc. of 0.1N iodine, I = the number of cc. of 0.05N thiosulfate required to offset the unexpended iodine, and N = the normality of the 0.05N thiosulfate solution.

XXIX. SOILS.

No additions or changes were made at the 1920 meeting.

XXX. REFERENCE TABLES.

No additions or changes were made at the 1920 meeting.

REPORT OF THE BOARD OF EDITORS.

By R. W. Balcom (Bureau of Chemistry, Washington, D. C.), *Chairman.*

In June, at the time of the taking over of the duties of the secretary-treasurer of the association as well as those of the chairman of its Board of Editors from Dr. Alsberg, the financial affairs of the association were those of a "going concern", but continued direction was necessary owing to the many unpaid bills and to the delay in the issuance of the May and August numbers of *The Journal* due to a printers' strike. The ad interim appointment was made by the Executive Committee

of the association. At this point it may be stated that the association owes a great deal to Miss Nellie A. Parkinson for her loyalty to the association as evidenced by her continued interest in its work in the face of great difficulties.

With the utmost endeavor it was impossible to get the May number of *The Journal*, Number 4 of Volume IV, mailed before the end of August. The August number, Number 1 of Volume V, which begins the proceedings of last year's meeting, is now ready. It is hoped that the November number will issue sometime in December and that the February 1922 number, in which publication of the proceedings of the present meeting will begin, will issue practically on time.

All bills received, including all expenses in connection with the first edition of 3000 copies of the Book of Methods, have been paid with the exception of the printer's bill of $1643.85 for Number 4 of Volume IV of *The Journal*. To do this it was necessary to draw upon subscriptions to Volumes V, VI, and VII, already paid in, to the extent of $938.75. There is due the association, and probably in large part collectable, subscriptions to Volume III of *The Journal*—$22.61; to Volume IV—$173.71; and for copies of the Book of Methods—$977.88, or a total of $1174.20. On October 15, when the books were closed, the deficit faced by the association—$1643.85 plus $938.75 less $1174.20 and less available bank balances of $461.78—was $946.62 or, in round numbers, $950.00. The purpose of preparing this statement is to show exactly the financial condition of the association. A similar statement next year will show how much progress, if any, has been made in wiping out this deficit. The suit brought by the Williams and Wilkins Company, former publishers of *The Journal*, has been dismissed, and it is for the association to decide what further action should be taken in that matter.

The first edition of the Book of Methods, with the exception of a few copies, has been sold. In spite of the large initial cost, the Book of Methods has more than paid for itself, and the demand has been most gratifying from other countries as well as our own. To fill future orders, 1000 additional copies have been run off.

The mailing list for the February issue showed 715 subscriptions to *The Journal;* by the end of August, at which time the May number issued, this number had been increased to 830. From August to October 15, mainly through circularization of those who had purchased the Book of Methods and were not at the same time subscribers to *The Journal*, the additional subscriptions secured increased the number on our mailing list to 868. Of these subscriptions 782, including 30 Canadian, are domestic. The remaining 86, or approximately 10 per cent, are foreign, distributed as follows: Africa, 14; Australia, 9; Brazil, 3; Chile, 1; China, 4; Denmark, 1; Egypt, 1; England, 20; France, 2; Germany, 2; Holland, 2; India, 12; Ireland, 4; Italy, 2; Japan, 1; Mexico, 1; Norway, 1;

Scotland, 5; West Indies, 1. This demand from other countries for *The Journal* and the Book of Methods shows how highly the work of the association is regarded outside of those countries to which membership is limited. The evidence of this regard is something of which the association may justly be proud and it should serve as an additional incentive to the exercise of its best efforts.

More subscriptions to *The Journal* are needed. The subscription list will have to be materially increased to make *The Journal* self-supporting, even when every effort has been made to hold the cost of production to a minimum and to obtain as much revenue as practicable from advertisements. Now that it is possible to publish the proceedings promptly subscriptions may be more freely solicited than has heretofore been the case, and every member of the association is urged to do everyting in his power to increase the subscription list. The members should realize that *The Journal* is the enterprise of the Association as a whole and not merely of its Board of Editors. If the element of personal responsibility is appreciated and assumed, it is believed to be entirely possible that at the next year's meeting a surplus instead of a deficit will be reported. Those who are now depending upon the libraries, including those who place the orders for these libraries, might well send in a personal subscription. A telling point is that *The Journal* gives a complete record of the work of the association, including any modifications of the official methods of analysis or additions thereto adopted at its annual meetings. These changes constitute the basis for the revision, from time to time, of the association's Book of Methods and subscription to *The Journal* is necessary to keep in close touch with the association's work.

Every effort should be made by those presenting reports and papers to make them as concise as may be consistent with clarity. When submitted they should be in final shape for publication. Illustrations should be suitably prepared for reproduction and particular attention should be given to see that appropriate legends accompany each table and that literature references are complete and accurate. Careful attention to these matters will expedite the editorial work and help to cut down the cost of publication. If there is any doubt in the mind of an author as to the form in which his report should be prepared, reference to his files of *The Journal* will probably give the desired information. It is the feeling of the Board of Editors that addresses, referees' reports, and other papers presented before the association should be considered the property of the association, and now that there will be no great delay in the publication of these papers in our own journal, it is believed that it will be sufficient to direct the attention of the members to the fact that advance publication of any of this material in other journals, except possibly in abstract form, is not to the best interest of this association.

Space should soon be available in *The Journal* for the publication of contributed articles along the lines of work the association is pursuing in addition to such papers and reports as are usually included in the proceedings.

R. N. Brackett.—I move the acceptance of this report of the Board of Editors with commendation.

The motion was seconded and carried.

R. W. Balcom.—At the 1915 meeting, a Board of Editors of *The Journal* to consist of the secretary of the association as chairman and four members to serve one, two, three and four years, respectively, each following appointment to be for four years, was authorized. The duties of the chairman have been and are likely to continue to be those of a managing editor. It is my belief, and this belief is shared by the Executive Committee, that the time has come when these editorial duties should be borne by someone other than the secretary of the association. There are several reasons for this, the controlling one of which is that the work of the Chairman of the Board of Editors as managing editor demands so much time that it should no longer be required of the secretary when he is at the same time one of the superior officers of any of our organizations; and the second is that eventually editorial policy and decisions are likely to be the subject of criticism, particularly when it is necessary to decide whether a contribution offered for publication in *The Journal* shall be accepted or rejected. No editorial staff can escape a certain amount of such criticism. The advantage of having these two offices separate is that when the association becomes dissatisfied with the way its *Journal* is being conducted, it can change its managing editor without the secretaryship being at the same time involved. In order to bring the matter before the association, on behalf of the Executive Committee, I wish to move that the secretary of the association be no longer required to serve as Chairman of the Board of Editors, and that a Chairman of the Board of Editors be elected as are the other members of the Board, for a period of four years.

The motion was seconded and carried.

No report was made by the Committee on Quartz Plate Standardization and Normal Weight.

REPORT OF COMMITTEE ON VEGETATION TESTS ON THE AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG.

By H. D. HASKINS (Agricultural Experiment Station, Amherst, Mass.), *Chairman.*

It is regretted that your committee is not able at this time to make a full report to the association. However, a brief review of the work that has been done both in pot and field will be given. The form in which the committee will make its final report for publication is still in doubt because all the members of the committee have not been consulted. A meeting of the committee was called at this convention, but W. B. Ellett of Virginia was the only member, besides the chairman, who was able to be present. Part of the summaries showing the results of the vegetation work, particularly of the pot vegetation work, have been prepared. A lot of extremely good work has been accomplished in these vegetation experiments, and it is hoped that the final results may be published in *The Journal,* and that there may be some discussion with reference to this point following this report. If there are any instructions which the association wishes to make to the committee they will be very acceptable.

Ten different experiment stations have undertaken and completed work on the availability of phosphoric acid in basic slag. They comprise the following: The Hawaiian Station, Illinois, Massachusetts, New Jersey, New York, North Carolina, North Dakota, Pennsylvania, Rhode Island and Texas. The total number of pot experiments conducted was 84, comprising 1,731 different pots. In the field work only three institutions found it possible to do any collaborative work. These results showed that 12 different experiments were conducted, including 332 tests on plots, making a total of 96 experiments, including pot and field work, with 2,063 different tests in both forms of experiment. That is a mass of data.

The result of the vegetation pot work has been satisfactory because it was possible for most of the collaborators to select soils that were known to be deficient in available phosphoric acid.

The vegetation field work did not give as satisfactory results as the pot work, for the reason, apparently, that the preliminary work was not conducted for a sufficient length of time properly to deplete the soils of available phosphoric acid in preparation for the final test. It may be said, however, that the vegetation field work does not emphasize any inferiority of the phosphoric acid furnished by the slags.

(A summary of both pot and field tests, showing the average yield of crop and phosphoric acid recovered by each phosphate, also the standing of each phosphate on the basis of increase in yield over no

phosphate pots and plots was then given. These figures were placed on a blackboard and are not reproduced here as they will form a part of the final report to the association which will be published in a later issue of *The Journal.*)

Your committee reports the following conclusions:

(1) That sufficient experimental work has been done, particularly along the line of vegetation pot work, to establish the fact that the phosphoric acid in the four slags under experiment was freely available to the crops grown; (2) that the results shown compare favorably with those obtained with acid phosphate, both from the standpoint of yield of crop as well as in phosphoric acid recovered; (3) that the tentative Wagner method when used on basic slag phosphates gives about the same proportion of available phosphoric acid in this class of products as does the official neutral citrate of ammonia method when used on acid phosphate or superphosphate, and that both methods give results which compare favorably with results obtained by the vegetation pot work.

It is the opinion of your committee that the tentative Wagner method is a reliable procedure for measuring the available phosphoric acid in basic slag phosphates and it would, therefore, recommend that it be adopted by the association as official.

It is also recommended that the detailed report of the Committee on Vegetation Tests on the Availabiltiy of Phosphoric Acid in Basic Slag be published in *The Journal* of the association as soon as it is completed and space is available.

H. D. HASKINS, B. L. HARTWELL,
J. A. BIZZELL, C. B. WILLIAMS.
W. B. ELLETT,

Committee on Vegetation Tests on the Availability of Phosphoric Acid in Basic Slag.

Adopted.

It was moved, seconded and adopted that the final report be published in concise form.

REPORT OF COMMITTEE TO COOPERATE WITH THE AMERICAN SOCIETY FOR TESTING MATERIALS.

The full membership of the committee was present at a meeting preliminary to a subsequent joint meeting with the two proper sub-committees of Committee C 7, of the American Society for Testing Materials. This meeting was held in Washington in the spring of 1921.

Your committee desires to report as follows:

An understanding was reached to the effect that cooperation was desirable between these two organizations, insofar as agricultural lime products are involved.

It was agreed that uniformity of chemical analytical methods for use in production laboratories and official control laboratories would prove desirable.

It is pointed out that no provision is made in the methods of the A. O. A. C. for the analyses of lime products which are already under official regulation in some states.

RECOMMENDATIONS.

It is recommended—

(1) That further collaboration and cooperation be carried out with the American Society for Testing Materials.

(2) That the committee be continued and directed to give consideration to the preparation of methods for the analyses of lime products, as a special chapter, or the adaptation of methods now used for the determined constituents of lime products, as such may be now provided for in other chapters of the methods of the association.

W. H. MacIntire,
F. P. Veitch.
William Frear,
Committee to cooperate with the American Society for Testing Materials.

Adopted.

No report was made by the Committee on Revision of Methods of Soil Analysis.

REPORT OF COMMITTEE ON RECOMMENDATIONS OF REFEREES.

By R. E. Doolittle (Food and Drug Inspection Station, Chicago, Ill.). *Chairman.*

You have already received the reports of Subcommittees A, B and C on the recommendations made by the several referees. There is little to add to these reports. The work of these subcommittees is most important, not only in the consideration of analytical and other data submitted in support of the recommendations made by the referees, but also in the directing and planning of future work. This meeting has established a record for the number of referee reports received. Out of a total of 73 referees and associate referees, reports were received from all except three, and some of these did work but made insufficient prog-

ress to warrant a report. This I believe is a record. It is due, in my opinion, to the recommendation made by your Committee on Recommendations of Referees last year that insofar as possible specific subjects be assigned associate referees in order that the work of the association may be kept under better control and a continuity of work established on a problem under consideration until definitely completed.

The chairman of this committee desires to call to the attention of the referees the following matters which have come to his attention in connection with this work:

(1) That it is important that the chairman of the subcommittee submit at least three copies of his report to the chairman to which his report is to be sent, in order that each member of the subcommittee may have an opportunity to study the report before the date set for the meeting.

(2) That the report should be submitted at the earliest possible date in order that the members of the subcommittees may have time to give it full consideration.

(3) That it is necessary for referees and associate referees to begin work upon their subjects immediately on returning to their respective homes. It appears to be a common practice to postpone starting work until spring and then vacations come along, collaborators can not be obtained and everything is rushed through in the last few weeks before the annual meeting. Many of these difficulties could be avoided if the main subjects were taken up at once when the details of past actions and the present status are fresh in mind.

The chairman also wishes, in behalf of the committee, to express its appreciation and thanks to the referees and associate referees for the splendid work done during the past year and for the complete and well-prepared reports submitted.

Adopted.

REPORT OF COMMITTEE A ON RECOMMENDATIONS OF REFEREES.

By B. B. Ross (Alabama Polytechnic Institute, Auburn, Ala.), *Chairman*.

[Fertilizers (boric acid in fertilizers, preparation of ammonium citrate, nitrogen, potash, potash availability, precipitated phosphates, vegetation tests on availability of phosphoric acid in basic slag), inorganic plant constituents (calcium, magnesium, iron and aluminium in the ash of seed; sulfur and phosphate in the seeds of plants), water, tanning materials and leather, insecticides and fungicides, and soils (sulfur in soils).]

FERTILIZERS.

BORIC ACID IN FERTILIZERS.

It is recommended—

(1) That the Bartlett method be adopted as an official method for the determination of boric acid in fertilizers and fertilizer materials on account of its special adaptation to the analysis of samples which are relatively high in soluble phosphates or organic matter. (First recommendation for adoption as official method.)

Approved.

(2) That the Ross-Deemer method[1] be adopted as an official method for the determination of water-soluble boric acid in fertilizers and fertilizer materials on account of its special adaptation to the analysis of samples which are low in soluble phosphates and organic matter relative to the boric acid. (First recommendation for adoption as official method.)

Approved.

(3) That further work be done on both the Bartlett and Ross-Deemer methods, recommended as tentative, to determine the effect of insoluble boric acid and to study any modifications necessary to make both methods applicable to the determination of water-soluble, acid-soluble or total boric acid, as the case may require.

Approved.

PREPARATION OF AMMONIUM CITRATE.

With regard to the recommendation of the associate referee on the preparation of ammonium citrate solution the committee would state that objections to the final adoption of the proposed method as the exclusive official method have been presented to the committee by several members of the association, it being contended, among other objections, that the working details of the method are not sufficiently definite and explicit in certain particulars, and that it is essential that more definite detailed directions be given before final adoption of the method as official.

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 327.

The committee desires to commend the excellent work done by the associate referee in developing the method presented for adoption, but is of the opinion that it is desirable to embody fuller details in the outline of the method as presented before final action on the method is taken by the association.

NITROGEN

It is recommended—

(1) That the association continue the study of the Devarda method.

Approved.

(2) That a comparison of results be made with the suggested modified Kjeldahl-Gunning method, by H. C. Moore[1], for the determination of nitrate nitrogen in nitrates and fertilizers.

Approved.

POTASH.

It is recommended—

(1) That the method by Moore and Caldwell[2] which calls for the use of stronger alcohol in connection with the Lindo-Gladding method be further studied. This was recommended at the last meeting but no samples were sent out to collaborators.

Approved.

(2) That the "Centrifugal Method for Determining Potash", by Elmer Sherrill[3] seems to be applicable when a rapid determination for factory control is necessary, but can not compare with the Lindo-Gladding method as an official method. However, the method is worthy of consideration, and it is recommended that it be given a trial by the association.

Approved.

POTASH AVAILABILITY.

No report or recommendations.

PRECIPITATED PHOSPHATES.

It is recommended—

(1) That the determination of insoluble phosphoric acid in precipitated phosphates be carried out according to the present official method for the determination of insoluble phosphoric acid in fertilizers, with the exception that a 1-gram charge be employed. (First reading.)

Approved.

(2) That a perforated crucible and gentle suction be employed in the filtration of the citrate solution after treatment, and that a filter paper be employed that will insure a free and rapid filtration without allowing the finely divided particles to pass through. The following papers have been found satisfactory (and there may be others): S. & S. No. 597,

---

[1] *J. Ind. Eng. Chem.*, 1920, 12: 669.
[2] *Ibid.*, 1188.
[3] *Ibid.*, 1921, 13: 227.

Whatman No. 2, Whatman No. 1, Munktell's No. I-F, Munktell's No. 2 and Durieux No. 121. (First reading.)

Approved.

VEGETATION TESTS OF AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG.

The committee recommends the adoption of the following recommendation of the Committee on Vegetation Tests:

It is the opinion of your committee that the tentative Wagner method is a reliable procedure for measuring the available phosphoric acid in basic slag phosphates and it would, therefore, recommend that it be adopted by the association as official.

Approved.

INORGANIC PLANT CONSTITUENTS.

CALCIUM, MAGNESIUM, IRON AND ALUMINIUM IN THE ASH OF SEED.

It is recommended—

(1) That further work be done on the determination of calcium and magnesium in the ash of seeds.

Approved.

(2) That the method for manganese[1] as given in the report of the referee be adopted as official.

Approved.

(3) That further study be given to the determination of iron and aluminium in the ash of seeds.

Approved.

SULFUR AND PHOSPHATES IN THE SEEDS OF PLANTS.

The committee also recommends the adoption of the recommendation of the associate referee that the method for determining sulfur and phosphorus in the seeds of plants[2], as outlined in his report, be studied by the coming referee and various collaborators.

WATER.

The committee recommends the approval of the recommendations of the referee for the adoption of the following as tentative methods (on first reading):

(1) Method for the determination of iodine in the presence of chlorine and bromine[3].

Approved.

(2) Method for analysis of salt[4]—moisture, matters insoluble in water and matters insoluble in acid.

Approved.

(3) Method of reporting results[5].

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 467.
[2] *Ibid.*, 469.
[3] *Ibid.*, 381.
[4] *Ibid.*, 384.
[5] *Ibid.*, 385.

The committee also favors the adoption of the following recommendations:

(4) That the tentative method of reporting results[1] be dropped.

Approved.

(5) That the quantitative methods for the determination of small quantities of copper and zinc in waters[2] be studied during the next year.

Approved.

TANNING MATERIALS AND LEATHER.

It is recommended—

(1) That work be continued on the solubility of various soaps in different solvents and upon a method, probably first breaking up the soap by heating the leather with an acid, for the extraction of total soaps in leather.

Approved.

(2) That investigations of a direct method for the determination of tannin in tanning materials be continued.

Approved.

INSECTICIDES AND FUNGICIDES.

It is recommended—

(1) That the mercury-thiocyanate method for zinc oxide in zinc arsenite[3] be adopted as an official method. (First reading. Adopted as a tentative method in 1920.)

Approved.

(2) That the bromate method, procedures (1) and (2), for the determination of arsenious oxide in zinc arsenite[4] be adopted as an official method. (Second reading.)

Approved.

(3) That the official method for the determination of water-soluble arsenic in lead arsenate[5] be adopted as official for the determination of water-soluble arsenic in zinc arsenite. (Second reading.)

Approved.

(4) That the bromate method[6] be adopted as an official method for the titration of the acid distillate in the official distillation method for the determination of total arsenic. (Second reading.)

Approved.

(5) That no further study be made of the modified Gooch and Browning method[7] for the determination of total arsenic in calcium arsenate.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 38.
[2] *J. Assoc. Official Agr. Chemists*, 1922, 5: 382.
[3] *J. Assoc. Official Agr. Chemists*, 1922, 5: 392.
[4] *Ibid.*, 394.
[5] *Assoc. Official Agr. Chemists, Methods*, 1920, 59.
[6] *J. Assoc. Official Agr. Chemists*, 1922, 5: 394.
[7] *Ibid.*, 395.

(6) That the bromate method, procedures (1) and (2), for the determination of arsenious oxide in calcium arsenate[1] be adopted as an official method. (Second reading.)

Approved.

(7) That method (1) for the determination of calcium oxide in calcium arsenate[1] be adopted as an official method. (First reading. Adopted as a tentative method in 1920.)

Approved.

(8) That method (2) for the determination of calcium oxide in calcium arsenate[2] be adopted as an official method. (First reading. Adopted as a tentative method in 1920.)

Approved.

(9) That in the "General procedure for the analysis of a product containing arsenic, antimony, lead, copper, zinc, iron, calcium, magnesium, etc.", the methods for lead oxide and copper[3] be adopted as official methods. (Second reading.)

Approved.

(10) That in the "General procedure for the analysis of a product containing arsenic, antimony, lead, copper, zinc, iron, calcium, magnesium, etc.", the method for zinc oxide[3] be adopted as an official method. (First reading. Adopted as a tentative method in 1920.)

Approved.

(11) That further action on the official distillation method for the determination of total arsenic in London purple be deferred until the suggested modification[4] has been studied.

Approved.

(12) That the zinc oxide-sodium carbonate method[5] be adopted as an official method for the determination of total arsenic in London purple. (Second reading.)

Approved.

(13) That the bromate method, procedures (a) and (b), for the determination of arsenious oxide in Paris green[6], as given in the referee's report in 1920, be adopted as an official method. (Second reading.)

Approved.

(14) That no further work be done at this time on magnesium arsenate.

Approved.

(15) That the words "Not applicable in presence of nitrates" be placed over the present distillation method for total arsenic wherever it occurs among the methods of the association.

Approved.

(16) That the distillation method for total arsenic in the presence of

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 395.
[2] *Ibid.*, 396.
[3] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 398.
[4] *Ibid.*, 402.
[5] *Ibid.*, 1921, **4**: 397.
[6] *Ibid.*, 399.

nitrates[1] suggested by Graham and Smith be adopted as a tentative method, with a view to its adoption as an official method after it has been further tested by cooperative work.

Approved.

(17) That the work on insecticides and fungicides for 1922 be a study of the distillation method mentioned in Recommendation 16 for the determination of arsenic in the presence of nitrates.

Approved.

SOILS.

It is recommended that during the ensuing year a further study be made of the method of determining sulfur in soils which is described in detail in the referee's report[2].

J. W. Kellogg: I believe it would be a splendid thing if a committee on fertilizer definitions and the interpretation of those definitions or of terms could be appointed. As you perhaps are aware, there is a Feed Control Officials' Association which has done a great deal of progressive work along this line. The 35 or 40 different definitions which have been adopted are a great help to us in interpretation of what these feeding stuffs materials are. It has been a great guide in that work. Now, I do not believe there is any need for a separate fertilizer officials' association, but we ought to get a little closer together on fertilizer work, not on method analysis of course, but on an agreement as to what certain by-products are and how they shall be listed and named in registration, and we might also define a fertilizer. It might be well to call it a special fertilizer committee—a fertilizer section—where the men who are specially interested could get together. It would expedite the work and agreement as to what some of these terms mean. Uniform methods of registration of fertilizer materials might be considered. There are about as many different kinds of registration blanks as there are States. We have the same trouble in feeding stuffs work and of course there is great confusion in meeting the requirements of the different States. There appears to be no uniformity as to how these blanks shall be submitted to the different departments. The methods of labelling sacks are different in the different States, and that is a source of confusion, not only to the manufacturer, but to the fertilizer control officials.

I would like to hear from others who are interested in this subject, and I am willing to make a motion that a committee or a section be appointed. I know that we already have a committee on food definitions; that does not consider methods of analysis at all, but decides on uniform terms, uniform interpretations of results.

E. G. Proulx: I heartily agree with what Mr. Kellogg has said on this subject. Undoubtedly, if you once start in you will find that there will

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 402.
[2] *Ibid.*, 405.

be sufficient problems to keep a committee busy. For many reasons I believe it would be better for this work to be done as a committee of this association instead of starting a separate association of fertilizer control officials.

H. A. Huston: You might legislate a lot of good chemists out of a job that way. At the present time it requires a pretty expert man to keep up with these laws. If you make it so uniform and so simple that the office boy can do it, a lot of chemists will be out of a job.

G. S. Fraps: I agree with Mr. Kellogg on some phases of this, but it seems to me there are some points which we ought to consider. In the first place, this organization is composed of official chemists, and not of control officials. Many of the chemists have no control over the marking of sacks or other things of that kind, and they really might not be in a position to discuss these things and commit themselves in the absence of the commissioner of agriculture, or whoever has charge of the fertilizer law. That is a point we ought to consider in connection with naming a committee to cover some of those things.

The matter of definitions of fertilizer terms might well be taken up but I doubt right now if a committee should be appointed as broad as the one Mr. Kellogg has named. It would hardly be possible for chemists who do not have authority to undertake to make rules for their respective departments in the absence of the supervisory officer. If sufficient number can secure authority then they could go ahead and do it. I do not think we ought to have a separate fertilizer section yet.

After further discussion a motion was made, seconded and carried that a Fertilizer Committee on Definitions of Terms and Interpretation of Results consisting of five members be appointed.

Later the president named the following committee: H. D. Haskins, J. W. Kellogg, E. G. Proulx, G. S. Fraps and R. N. Brackett.

REPORT OF COMMITTEE B ON RECOMMENDATIONS OF REFEREES.

By Hermann C. Lythgoe (State Department of Public Health, Boston, Mass.), *Chairman*.

[Foods and feeding stuffs (crude fiber, detection of reground bran in shorts, stock feed adulteration), saccharine products (sugar, honey, maple products, maltose products, sugar-house products), dairy products (moisture in cheese, fats and oils), baking powder, chemical reagents, eggs and egg products, drugs.]

FOODS AND FEEDING STUFFS.

It is recommended—

(1) That a further study be made of sulfur dioxide and chlorine in bleached grain.

Approved.

(2) That the method for determining the acidity of corn, as specified by Black and Alsberg[1], be considered by the referee next year with a view to its adoption as an official method, and that the method be studied to see if changes are necessary to make it applicable to grains other than corn.

Approved.

(3) That the referee study the existing official general methods[2] for water in foods and feeding stuffs with a view to rewording and fixing rigidly the conditions of temperature, pressure and other factors.

Approved.

(4) That a definite method applicable to the determination of water in dried food be designed and submitted to the association

Approved.

(5) That the referee study methods of determining ether extract in various foods and feeding stuffs the coming year, with a view to ascertaining whether or not the official method for the determination of ether extract is applicable to all the products for which it is now being used.

Approved.

CRUDE FIBER.

It is recommended—

That the present official method[3] be deleted and the one proposed by the referee[4] be substituted. (First reading.)

Approved

REGROUND BRAN IN SHORTS.

It is recommended—

That the work on this subject be discontinued.

Approved

STOCK FEED ADULTERATION.

It is recommended—

(1) That the microscopic method for the determination of rice hulls in rice bran[5] be adopted as tentative

Approved.

(2) That further study of methods for the estimation of grit in poultry and similar foods be continued.

Approved.

(3) That further study be employed for the estimation of bone in meat scraps.

Approved.

(4) That further study of microscopic methods for the examination of mixed foods be employed.

Approved.

---

[1] U. S. Bur. Plant Ind. Bull., 199: (1920).
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 71.
[3] *Ibid.*, 97.
[4] *J. Assoc. Official Agr. Chemists*, 1922, 5: 421.
[5] *Ibid.*, 77.

SACCHARINE PRODUCTS.

SUGAR.

It is recommended—

(1) That the modifications proposed in 1916 for determining sucrose by acid and invertase inversions be further studied.

Approved.

(2) That the work upon determining small amounts of reducing sugars in the presence of sucrose be continued.

Approved.

HONEY.

It is recommended—

That the work on resorcin and aniline chloride tests for the detection of invert sugar sirup in honey[1] be further studied in connection with honey heated to a comparatively high temperature. It is suggested that directions to collaborators be more specific as to details of technique and color.

Approved.

MAPLE PRODUCTS.

It is recommended—

That further study be made of the Canadian lead number and the conductivity value.

Approved.

MALTOSE PRODUCTS.

It is recommended—

That the work begun by the referee be continued.

Approved.

SUGAR-HOUSE PRODUCTS.

It is recommended that the following recommendations which were made in 1919 be continued—

(1) That a study be made of the influence of different and known temperatures of incineration on the results of ash determinations in cane sirups and molasses, carrying out the incineration in both platinum and silica dishes for comparison.

Approved.

(2) That as large a number as possible of samples of different grades of cane sirups and molasses be used for preparing ash determinations by the sulfate and direct methods, to determine, if possible, the proper correction factor to be applied to the sulfate ash.

Approved.

(3) That a comparative study of methods for the determination of specific gravity and of total solids of molasses be undertaken.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 112; *J. Assoc. Official Agr. Chemists*, 1922, **5**: 429.

DAIRY PRODUCTS.

It is recommended—

(1) That the cryoscopic method for the examination of milk[1] be adopted as official. (First reading.)

Approved.

(2) That the neutral method for fat in malted milk as outlined by the referee be further studied during the coming year. (This takes the place of recommendations 1, 2 and 3 of 1920.)

Approved.

(3) That the Schmidt-Bondzynski method[2] for fat in cheese be adopted as official. (Second reading; first reading in 1917.)

Approved.

(4) That the referee study the proposed change in the official method for the determination of fat in unsweetened condensed milk[3], suggested by J. T. Kiester, and report at the next meeting.

Approved.

MOISTURE IN CHEESE.

It is recommended—

(1) That the present tentative method for moisture in cheese[4] be rewritten to include:

(a) That either 10 to 15 grams of sea-sand or 2 to 3 grams of asbestos be used; and

(b) that the sample be dried in a vacuum, or at atmospheric pressure at the temperature of boiling water; and

that this method be further studied with the view of making it official

Approved.

FATS AND OILS.

It is recommended—

(1) That the Wijs method[5] for the determination of iodine absorption number be made official. (Final action.)

Approved.

(2) That the alternative method for the preparation of Wijs solution be adopted.

Approved.

(3) That further study on the Hanus method[6] be made as to length of time of absorption.

Approved.

(4) That the referee confer with the Society on Testing Materials in order that the methods may be uniform with those of the society.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 178.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 235.
[3] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 509.
[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 234.
[5] *Ibid.*, 245.
[6] *Ibid.*, 244.

(5) That further study on the determination of sesame oil be made along the lines suggested by the referee.

Approved.

BAKING POWDER.

It is recommended—

(1) That the Chittick method[1] as modified for the determination of lead in baking powder be adopted as tentative.

Approved.

(2) That further study of the electrolytic method[2] for the determination of lead in baking powder be made.

Approved.

(3) That the use of different indicators or a combination of indicators be studied in connection with the determination of the neutralizing strength of phosphates used in the manufacture of baking powder.

Approved.

(4) That collaborative study be made on the determination of fluorine in baking powder.

Approved.

(5) That further study of volumetric methods for the determination of carbon dioxide in baking powder be made.

Approved.

CHEMICAL REAGENTS

It is recommended—

(1) That the recommendation of the referee regarding specifications of metric units be referred to the Committee on Resolutions.

Approved.

(2) That the following recommendations of 1920 be reported:

> (1) That this association declare itself in favor of cooperating with the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society in the collection of data in regard to the quality of reagents on the market.
>
> (2) That the secretary of this association be instructed to transmit a statement of this action to the proper official of each institution represented in the membership of the association and request that the purchasing agent or some other official of the institution send him a carbon copy of each letter written to a manufacturer or dealer calling attention to a specific instance of delivery of an unsatisfactory reagent.

Approved.

EGGS AND EGG PRODUCTS.

It is recommended—

That the report of the referee be accepted and published in the proceedings, and that the methods proposed be studied collaboratively before adoption as tentative or official.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 514.
[2] *Ibid.*, 1920, 4: 221.

The referee on eggs and egg products moved that the recommendation of the committee be amended to provide that the methods submitted in the referee's report be adopted as tentative methods.

The amendment was lost.

DRUGS.

ACETYLSALICYLIC ACID[1].

It is recommended—

(1) That the method suggested for the determination of the melting point be compared with the method adopted by the association and reported upon next year.

Approved.

(2) That the qualitative test for free salicylic acid, as described by the referee, be adopted as a tentative method.

Approved.

(3) That the quantitative method for salicylic acid, substantially as described by the referee but including the details suggested by H. O. Moraw, be made a tentative method, and that same be resubmitted to collaborators by next year's associate referee with a view to its adoption as an official A. O. A. C. procedure.

Approved.

(4) That the iodine method for total salicylates, as described in the recommendation, be made a tentative method, and that same be further tried out by next year's associate referee with a view to its final adoption as an official method.

Approved.

(5) That the bromine method for total salicylates, as described in the recommendation, be made a tentative method, and that same be further tried out by next year's associate referee with a view to its final adoption as an official method.

Approved.

(6) That the double titration method for acetylsalicylic acid, as described in the recommendation, be made a tentative method, and that same be further tried out by next year's associate referee with a view to its final adoption as an official method.

Approved.

(7) That A. Nutter Smith's method for free acetic acid and any other available methods for this determination be submitted to collaborative study by next year's associate referee.

Approved.

(8) That consideration be given to methods for the quantitative determination of combined acetic acid in acetylsalicylic acid.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 581.

(9) That the problem of determining aspirin in the presence of possible interfering substances be given consideration by next year's associate referee.

Approved.

PHENOLPHTHALEIN.

It is recommended—

That an associate referee be appointed to continue the study of methods for the examination of phenolphthalein.

Approved.

CAMPHOR.

It is recommended—

That the methods[1] suggested for the determination of camphor in pills and tablets be further studied during the coming year.

Approved.

MONOBROMATED CAMPHOR.

It is recommended—

That the methods[2] submitted be adopted as tentative and that further study be made of these methods during the coming year.

Approved.

MERCURY.

It is recommended—

That an associate referee be appointed to study the methods for the examination of mercurous chloride, mercuric chloride and mercuric iodine already reported to the association, or such methods as may be available elsewhere for the purpose of developing a satisfactory method.

Approved.

TURPENTINE OIL[3].

It is recommended—

(1) That the fuming sulfuric acid method be further studied with special attention to the preparation of the reagent and to the details of the process.

Approved.

(2) That the sulfuric-nitric acid method be further studied.

Approved.

(3) That additional methods be studied in comparison with the methods already studied.

Approved.

PAPAIN.

It is recommended—

That for the present studies on papain be discontinued.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 544.
[2] *Ibid.*, 587.
[3] *Ibid.*, 547.

ALKALOIDS[1].

SEPARATION OF QUININE AND STRYCHNINE.

It is recommended—

That the method submitted for the separation of quinine and strychnine be made tentative. (First reading.)

Approved.

PHYSOSTIGMA.

It is recommended—

That the method for the assay of physostigma and its preparations be made a tentative method. (First reading.) It was recommended by the associate referee that this method be adopted as official, but it differs from the U. S. P. method.

Approved.

EXTRACT OF HYOSCYAMUS.

It is recommended—

That the method for the assay of extract of hyoscyamus and its preparations be made a tentative method. (First reading.) It was recommended by the associate referee that this method be adopted as official, but it differs from the U. S. P. method.

Approved.

IPECAC.

It is recommended—

That the comparative study of the volumetric and gravimetric methods for the assay of ipecac be continued.

Approved.

BELLADONNA LINIMENT.

It is recommended—

That the methods submitted for the assay of the liniment of belladonna be further studied.

Approved.

STRAMONIUM.

It is recommended—

That a study be made on methods for assaying the ointment of stramonium.

Approved.

ATROPINE.

It is recommended—

That further studies be made on methods for the assay of atropine in tablets.

Approved.

STRYCHNINE.

It is recommended—

(1) That the method for the assay of strychnine in tablets, including the volumetric method, be adopted as an official method. (First reading.)

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 564.

(2) That the method for the assay of strychnine in liquids, including the volumetric method, be adopted as an official method. (First reading.)

Approved.

MORPHINE, CODEINE AND DIACETYLMORPHINE[1].

It is recommended—

(1) That the methods for the qualitative and quantitative determination of morphine, codeine and diacetylmorphine be adopted as tentative methods. (First reading.)

Approved.

(2) That these methods be further studied with a view to making them official.

Approved.

SYNTHETIC PRODUCTS.

It is recommended—

(1) That Recommendations 1, 2 and 3 under synthetic products for 1920[2] be dropped, since Recommendations 2 and 3 have been taken care of under other subjects and there are satisfactory methods available under No. 1.

Approved.

PROCAINE[3].

(1) That the methods submitted be further studied during the coming year with a view to making them provisional.

Approved.

MEDICINAL PLANTS[4].

The methods for the macroscopic and microscopic identification of certain drugs have been reported, with the results of collaborative study thereon. Inasmuch as such methods represent a radical departure from the practice of this association, it is recommended—

(1) That these be referred to the Committee on Revision of Methods for consideration before any action is taken. The committee, however, recommends that these methods should be published in *The Journal*.

Approved.

(2) That the study of volume weight of medicinal plants be continued with the assistance of collaborators.

Approved.

(3) That the study of the sublimation of plant products be continued with the assistance of collaborators.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 573.
[2] *Ibid.*, 1921, 4: 573.
[3] *Ibid*, 1922, 5: 589.
[4] *Ibid.*, 560.

SANTONINE.

(4) That the tentative method for the detection of santonine in wormseed be studied by collaborators with the view of making it official.

Approved.

POLLEN GRAINS.

(5) That the method for the use of pollen grains as a means of identification of plants and plant products be further studied.

Approved.

BITTER TONIC AND LAXATIVE DRUGS[1].

It is recommended—

(1) That the gravimetric method evolved for assaying the anthraquinone drugs be given a more exhaustive study during the coming year.

Approved.

(2) That conjointly with the study of gravimetric assay, the collaborative work be extended to the colorimetric determinations.

Approved.

(3) That the method for estimating aloin be submitted to the association for study and criticism.

Approved.

ARSENICALS[2].

It is recommended—

(1) That the qualitative and quantitative methods submitted be adopted by the association as tentative methods, and that they be further studied during the next year with a view to their official adoption.

Approved.

(2) That the modification suggested by H. Engelhardt, which provides for digestion with potassium permanganate, addition of potassium iodide, discharge of liberated iodine by use of sodium sulfite solution, and final titration with 0.1N iodine solution, be studied during the next year.

Approved.

(3) That during the next year the associate referee should study and devise methods to determine the arsenic to nitrogen ratio in arsphenamine and neoarsphenamine.

Approved.

(4) That methods for the detection of organic sulfur in arsenicals be further studied.

Approved.

(5) That methods be outlined for the detection of toxicity tolerance of arsphenamine and neoarsphenamine.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 575.
[2] *Ibid.*, 527.

SANDALWOOD OIL[1].

It is recommended—

That the methods submitted and studied by C. W. Harrison for the determination of the acetyl value of sandalwood oil be further studied.

Approved.

GUMS AND BALSAMS.

It is recommended—

That work on gums and balsams carried forward since 1919 be discontinued on account of difficulty of obtaining workers.

Approved.

SILVER PROTEINATES.

It is recommended—

That further work be carried out on Method 3[2].

Approved.

ALCOHOL IN DRUGS.

It is recommended—

That the method for the determination of alcohol in drugs be further studied.

Approved.

SPECIFIC GRAVITY TABLES.

The referee recommended that those portions of the report dealing with the specific gravity tables be referred to the Committee on Revision of Methods. Your committee, after further consideration, recommends that this question be referred to a special committee to be appointed by the incoming executive committee.

Approved.

CHLOROFORM AND CHLORAL HYDRATE.

It is recommended—

(1) That the method for the determination of chloroform be further studied.

Approved.

(2) That no further work be done on chloral hydrate.

Approved.

CINCHONA ALKALOIDS.

It is recommended—

That further study be made on the separation of the principal cinchona alkaloids.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 545.
[2] *Ibid.*, 543.

REPORT OF COMMITTEE C ON RECOMMENDATIONS OF REFEREES.

By R. E. Doolittle (1625 Transportation Building, Chicago, Ill.), *Chairman.*

[Food preservatives (saccharin), coloring matters in foods, metals in foods (arsenic), fruit and fruit products (pectin in fruits and fruit products, moisture in dried fruit), canned foods, cereal foods, limits of accuracy in the determination of small amounts of alcohol in beers, vinegars, flavoring extracts, meat and meat products (separation of meat proteins, decomposition of meat products, gelatin), spices, cacao products (determination of shells, methods for the examination of cacao butter), coffee, tea, and nitrogen in foods.]

FOOD PRESERVATIVES.

SACCHARIN.

It is recommended—

(1) That the referee prepare a list of the methods now commonly used for the determination of saccharin in food products.

Approved.

(2) That the referee conduct collaborative work on those methods which yield good results as indicated by previous studies.

Approved.

COLORING MATTERS IN FOODS.

It is recommended—

(1) That the methods adopted tentatively at the 1920 meeting for the examination of coal-tar food colors[1] be submitted to collaborative study during the coming year with a view to their perfection for final adoption as official methods.

Approved.

(2) That the investigative work on the coloring matters of the common fruits and vegetables be continued.

Approved.

METALS IN FOODS.

It is recommended—

(1) That the modified Penniman method for the determination of tin[2], be submitted to further collaborative study during the coming year.

Approved.

ARSENIC.

It is recommended—

(1) That the H. V. Farr modification of the Gutzeit method for the determination of arsenic[3], be further studied with a view to

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 198.
[2] *Ibid.*, 6: 29.
[3] *Ibid.*, 31.

simplifying the apparatus and ascertaining the conditions necessary for a more accurate determination in concentrations above 20 micromilligrams of arsenious oxide (As_2O_3).

Approved.

(2) That the present tentative Gutzeit method[1] for the determination of arsenic be studied in comparison with the H. V. Farr modification.

Approved.

FRUITS AND FRUIT PRODUCTS.

PECTIN IN FRUITS AND FRUIT PRODUCTS.

It is recommended—

(1) That the referee begin a comprehensive study of the composition of fruits used in the manufacture of jam and jelly to determine the natural variations and to serve as a basis for interpretation of analytical results.

Approved.

(2) That further work be done on methods for the determination of total sulfur in fruits.

Approved.

(3) That the methods submitted by the referee this year be modified with respect to the period of boiling in the preparation of sample and the elimination of filter paper in the determination of total sulfur, and that the methods as modified be subjected to further collaborative study during the coming year.

Approved.

The referee further recommends—

(4) That the present method for the determination of alcohol precipitate be disregarded as it is unreliable.

Your committee recommends—

That inasmuch as modifications have been recommended for the methods as submitted by the referee this year action on the elimination of the method for the determination of alcohol precipitate be postponed until the substitute methods are in form for consideration for adoption by the association.

Report of committee adopted.

MOISTURE IN DRIED FRUIT.

It is recommended—

(1) That the method submitted by the referee for the determination of moisture in dried fruits[2] (for dried fruits in general), be adopted as an official method (first action) and submitted to further collaborative study during the coming year.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 147.
[2] *J. Assoc. Official Agr. Chemists*, 1922, **6**: 48.

(2) That the method submitted by the referee for the determination of moisture in dried apples only be adopted as a tentative method and submitted to further collaborative study during the coming year.

Approved.

(3) That an attempt be made to determine the moisture in dried fruits by some method depending upon a totally different principle as the calcium carbide method[1].

Approved.

CANNED FOODS

It is recommended—

(1) That the wording of the methods for the micro-analysis of tomato pulp, catsup, purée, sauce and paste[2] be changed to read as follows:

MOLDS.—TENTATIVE.

(*a*) **28**, *Paragraph 2.*

Place the slide under the microscope and examine with a magnification of about 90 diameters and with such adjustment that each field of view covers 1.5 sq. mm. This area is of vital importance and may be determined by adjusting the draw-tube in such a way that the diameter of the field becomes 1.382 mm. as determined by measurement with a stage micrometer. A 16 mm. Zeiss apochromatic objective with a Zeiss X6 compensating ocular or a Spencer 16 mm. apochromatic objective with a Spencer X10 compensating ocular, or their equivalents, shall be used to obtain this magnification. Under these conditions the amount of liquid examined is 0.15 cmm. (0.00015 cc.) per field.

YEASTS AND SPORES.—TENTATIVE.

(b) **29**, *Paragraph 3, line 4.*

After the expression "1/60 cmm." insert "(1/60,000 cc.)".

BACTERIA.—TENTATIVE.

(c) **30**, *Paragraphs 1 and 2.*

Estimate the number of rod-shaped bacteria from the mounted sample used in **29** but, before examination, allow the sample to stand not less than 15 minutes after mounting. Employ a magnification of about 500 which may be obtained by the use of an 8 mm. Zeiss apochromatic objective with an X18 Zeiss compensating ocular with draw-tube not extended, or an 8 mm. Spencer aprochromatic objective with an X20 Spencer compensating ocular and a tube length of 190, or their equivalents.

Count and record the number of bacteria having a length greater than 1½ times their width in an area consisting of five of the small sized squares. Count five such areas, preferably one from near each corner of the ruled portion of the slide and one from near the center. Determine the total number of rod-shaped bacteria in the 5 areas and multiply by 480,000. This gives the number of this type of bacteria per cc. If a dilution of 1 part of the sample with 8 parts of water, instead of 1 part of the sample with 2 parts of the water is used in making up the sample, then the total count obtained as above must be multiplied by 1,440,000. Thus far it has proved impracticable to count the micrococci present as they are likely to be confused with other bodies frequently present in such products.

Approved.

[1] U. S. Bur. Chem. Circ. 97: (1912).
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 164.

(2) That the methods for the micro-analysis of tomato pulp, catsup, purée, sauce and paste as corrected in wording be adopted as official methods. (First action.)

Approved.

CEREAL FOODS.

It is recommended—

(1) That collaborative work on the determination of cold water extract be discontinued.

Approved.

(2) That work on the determination of moisture and ash be discontinued until further research develops more desirable methods.

Approved.

(3) That the method submitted by the referee for the determination of fat in baked cereal products[1], be adopted as a tentative method and subjected to further collaborative study.

Approved.

(4) That the methods submitted by the associate referee for the determination of chlorine in chlorine bleached flours[2], be modified as suggested in his report and the modified methods subjected to collaborative study during the coming year.

Approved.

LIMITS OF ACCURACY IN THE DETERMINATION OF SMALL AMOUNTS OF ALCOHOL IN BEER.

No report was submitted by the referee.

It is recommended—

That these studies be continued.

Approved.

VINEGARS.

No report was submitted by the referee.

It is recommended—

That the methods for the determination of glycerol, solids and fixed acids be studied by the referee during the coming year.

Approved.

FLAVORING EXTRACTS.

No report was submitted by the referee.

It is recommended—

(1) That a study of methods for the analysis of imitation vanilla preparations containing large quantities of coumarin and vanillin be undertaken.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 6: 63.
[2] *Ibid.*, 68.

(2) That the method suggested by Penniman and Randall[1] for the determination of oil in lemon and orange extracts be studied in connection with the official method.

Approved.

(3) That a study of methods for the examination of non-alcoholic extracts be undertaken.

Approved.

(4) That the method adopted at the 1919 meeting of the association as an official method (first action) for the determination of alcohol in orange and lemon extracts consisting only of alcohol, oil and water[2] be subjected to collaborative study with a view to recommendation for final action.

Approved.

(5) That the official methods for the determination of citral in orange and lemon extracts and in orange and lemon oils[3] be investigated.

Approved.

MEAT AND MEAT PRODUCTS.

It is recommended—

(1) That the method for the determination of sugar in meats[4], receive further study.

Approved.

(2) That the modified method reported by the referee for the determination of nitrates and nitrites calculated as sodium nitrate[5], be substituted for the present ferrous chloride method for the determination of nitrates[6].

Approved.

(3) That the phenoldisulfonic acid method for the determination of nitrites and nitrates calculated as sodium nitrate, **XX**, **12** and **13**[7] be changed in the following particulars:

(a) **12** (b) lines 1, 5 and 7, substitute the word "sodium" for the word "potassium", making these lines read "sodium nitrate" in the place of "potassium nitrate".

(b) **13**, line 13, substitute the word "sodium" for the word "potassium", making the line read, "Determine the amount of sodium nitrate present in the sample by comparison".

Approved.

---

[1] *J. Ind. Eng. Chem.*, 1914, **11**: 926.
[2] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 308.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 201.
[4] *J. Assoc. Official Agr. Chemists*, 1922, **6**: 72.
[5] *Ibid.*, 74.
[6] *Assoc. Official Agr. Chemists, Methods*, 1920, 210.
[7] *Ibid.*, 211.

SEPARATION OF MEAT PROTEINS.

It is recommended—

(1) That further work be done concerning the relation of the concentration of acid and protein to the coagulation by salt of protein of meat soluble in cold water.

Approved.

(2) That zinc sulfate be compared with ammonium and sodium sulfates for the separation of meat proteins.

Approved.

(3) That further work be done with the sodium chloride and tannic acid method to determine all the conditions necessary to give comparable results.

Approved.

DECOMPOSITION OF MEAT PRODUCTS.

No report or recommendations.

GELATIN.

No report was submitted by the referee.

It is recommended—

That the tentative methods[1] adopted at the 1920 meeting be submitted to collaborative study during the coming year with a view to their perfection for final action by the association.

Approved.

SPICES.

It is recommended—

(1) That the present tentative method for the determination of volatile oil in mustard seed[2] be made official (final action).

Approved.

(2) That consideration be given to the recommendation of the referee for 1920 on spices and other condiments to study methods for the examination of salad dressings.

Approved.

(3) The referee further recommends a modified method for the determination of crude fiber in prepared mustard.

Your committee, in view of the action taken by the association dropping the official method under Foods and Feeding Stuffs for the determi-

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 343.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 259.

nation of crude fiber and the substitution therefor of a tentative method, recommends that action on the referee's recommendation be postponed and that the referee during the coming year study the newly adopted tentative method for the determination of crude fiber in prepared mustard and other spices.

Report of committee approved.

CACAO PRODUCTS.

DETERMINATION OF SHELLS.

It is recommended—

That the method given in the referee's report for 1920[1] be adopted as a tentative method for the quantitative determination of shells in cacao and chocolate products and that same be submitted to further collaborative study during the coming year with a view to its final adoption as an official method.

Approved.

METHODS FOR THE EXAMINATION OF CACAO BUTTER.

It is recommended—

That further study be given to the methods outlined in the report of the referee for 1920[2] for determining the critical temperature of dissolution and to the acetone-carbon tetrachloride test for hydrogenated oils, tallows, etc.

Approved.

COFFEE

It is recommended—

(1) That the Power-Chesnut method for the determination of caffeine in coffee[3] be modified to require the addition of 20 cc. of 10 per cent sulfuric acid instead of 10 cc. (line 10) for the half-hour boiling of the filtrate from the magnesium treatment and the method as thus modified be adopted as official. (Final action.)

Approved.

(2) That during the coming year the incoming referee study the acids in coffee.

Approved.

TEA.

It is recommended—

(1) That the Power-Chesnut method for the determination of caffeine in tea[4] be adopted as an official method. (Final action.)

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 253.
[2] *Ibid.*, 266.
[3] *Ibid.*, 271.
[4] *Ibid.*, 290.

(2) That the Bailey-Andrew method[1] for the determination of caffeine in tea be adopted as an official method. (First action.)

Approved.

(3) That the Stahlschmidt method[2] for the determination of caffeine in tea be dropped.

Approved.

(4) That suggestions for further study of the subject of tea be left to the incoming referee.

Approved.

NITROGEN IN FOODS.

No report was submitted.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 292.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 274.

THIRD DAY.

WEDNESDAY—AFTERNOON SESSION

REPORT OF REPRESENTATIVE TO COOPERATE WITH THE UNITED STATES PHARMACOPŒIAL REVISION COMMITTEE.

By L. F. Kebler (Bureau of Chemistry, Washington, D. C.), *Chairman*.

A resolution was passed last year by the drug section authorizing the appointment of a representative to cooperate with the Committee of Revision of the United States Pharmacopœia. The idea in mind then was the appointment of some State official to undertake the work so as to identify State bodies with the revision, but the writer was delegated to act in the matter and has kept in fairly close touch with the work and the progress made so far.

Since the appointment of the Committee of Revision in 1920 much progress has been made by way of outlining general policies to be followed, although many of these were formulated at the convention in that year.

The first important step is the selection of the drugs to be recognized by the Pharmacopœia. This task is the work of the Committee on Scope. A large number of drugs have been approved for inclusion in the next revision; some are under active consideration and discussion and some included in the 9th revision will be deleted.

Monographs have been written up for some of the drugs to be included; others are in course of preparation. The methods of analysis have been given in a number of cases. This work, which primarily interests this association, is about to assume definite form and the organization should take an active hand.

In the former edition of the Pharmacopœia efforts were made to adopt the best methods of analysis available. Such methods as had been worked out and adopted by this association received some attention, but it is believed that they would have received more consideration if this organization had been actively identified with the work of revision in some way.

It is recognized that the alcohol tables contained in the present Pharmacopœia differ in a number of material respects from the alcohol tables contained in the Association's official methods. The method for estimating alcohol prescribed for drug products in the Pharmacopœia differs somewhat from the methods outlined for food products. The same is true of the method for detecting adulterations in oil of turpentine. The

list could be multiplied but the instances of differences cited are sufficient to show the need of cooperation and coordination in order to bring about a more satisfactory condition for the chemist. It is inadvisable to have two official methods of analysis. The methods in the Pharmacopœia are legal under the Food and Drugs Act, and those contained in the Methods of Analysis of the A. O. A. C. are made official by regulation.

It is sometimes contended that the methods in the Pharmacopœia are unworkable; that they are intended for certain classes of people and that they do not give the best results or conclusions. It is the duty of every analyst to bring to the attention of the Committee of Revision of the United States Pharmacopœia the inaccuracies or shortcomings of any methods of analysis or procedure so that they may be adjusted or eliminated in the next revision.

In order to place this work on a more satisfactory basis and to give representation to those who most frequently use the methods of analysis, both United States Pharmacopœia and those of the Association of Official Agricultural Chemists, it is recommended that a committee of five be appointed to represent this association in the matter of cooperating with the Committee of Revision of the Pharmacopœia. By means of such a committee a definite working relation can be established between this association and the Committee of Revision through its chairman. It is believed that such a committee would be able to bring much useful information to the attention of the Committee of Revision and be instrumental in having it incorporated into the book which will become the legal standard, not only under the Federal law but under State laws.

Adopted.

H. C. Lythgoe: Relative to Dr. Kebler's report, I have had handed to me a copy of a motion made and carried in the drug section, which reads as follows:

In view of the fact that the standards for drugs recognized in the United States Pharmacopœia are legalized by Federal and State laws, it seems advisable that the Association of Official Agricultural Chemists should cooperate with the proper committees on the United States Pharmacopœia revision. I therefore move that a committee of three members of this association be appointed whose duty it shall be to cooperate with the officials of the Committee of the Revision of the Pharmacopœia with regard to the methods of analysis of drugs, and that the committee be directed to report at the next meeting of the association.

The motion was seconded and carried.

Later this motion was amended changing the number to serve on the committee from three to five, and the chair accordingly appointed the following members: L. F. Kebler, chairman; H. C. Lythgoe; H. C. Fuller; A. R. Bliss and W. S. Hubbard.

The amendment was accepted and carried.

REPORT OF REPRESENTATIVES ON THE BOARD OF GOVERNORS OF THE CROP PROTECTION INSTITUTE OF THE NATIONAL RESEARCH COUNCIL.

H. J. Patterson: The following report was prepared by B. L. Hartwell, chairman, but the work of the committee has been so limited that we invited H. E. Howe of the National Research Council[1] to come and tell in greater detail of the aims of the institute.

Since this association has been represented on the Board of Governors of the Institute only since June, it is desirable to state that the institute, as its name indicates, is concerned with the protection of crops from their afflictions, by agencies not interfering with other organized efforts.

It is managed for the public good, by a Board of Governors of nine or more representatives of appropriate scientific societies, together with a Board of Trustees from the industries naturally concerned.

Projects receive consideration, approval and direction by the Board of Governors after consultation with the Board of Trustees.

At present the secretary and the treasurer are the same persons who hold these offices in the National Research Council.

The annual dues for scientific members are $1, for industrial members $100, and for associate industrial members $10.

Any funds required for the pursuit of specific projects are secured by the trustees of the industrial divisions concerned.

Some of the work of this association and of the institute will have to do with the same projects; the institute with investigations concerning the adaptation of materials—such as insecticides and fungicides, for example—for special purposes, as a basis for claims made by the manufacturers; and the association in connection with the inspection of the materials and concerning the validity of the claims which accompany the commercial products.

It seems obvious that one important function of the institute will be to act as a clearing house for the transmission of ideas from any interest concerned in the economics of vegetable food from the beginning of its production to the time of its consumption.

Until after an opportunity to attend meetings of the institute, your committee can not undertake to acquaint you with specific projects, but will welcome suggestions needing consideration by the Board of Governors.

H. E. Howe: I am to give you a brief progress report on the Crop Protection Institute in which you have representation. This Crop Protection Institute came about through a desire of the entomologists and phyto-

[1] Present address, Journal of Industrial & Engineering Chemistry, 810 Eighteenth St., N. W., Washington, D. C.

pathologists for some way in which they could cooperate in certain classes of research work with industry. A great many of the men concerned were engaged on such work that they could not travel outside the confines of their own states, except at their own expense, and it was obviously desirable to bring together these gentlemen for various types of conferences, particularly with regard to regional research work. The manufacturers of insecticides, fungicides and similar materials seemed to be quite willing to support progressive work of this kind, but had no direct way in which to do it to their own satisfaction. We found upon investigation that many of these groups really had never worked together, and there seemed to be a little suspicious atmosphere which we were anxious to dispel. We endeavored to bring together this group first here in Washington, and later in New York City, to decide what might be done. At the conference here in Washington Dr. Alsberg, Dr Haywood and others, who were interested in the chemical side of the problem, were present. We were very glad to bring into this work this association and any others who might be interested in the general purposes that were under consideration. I think the constitution and bylaws as well as the report of work to date may have reached many of you through the first bulletin prepared by the institute. I will just read one or two paragraphs.

The purposes of the Institute are:

(4) To further cooperation between scientific workers and the manufacturers of insecticides, fungicides and other similar materials, the manufacturers of appliances required for their use, and the manufacturers, packers and shippers of plant, animal and other products.

(5) To assist in the dissemination of scientifically correct information regarding the control of injurious insects and plant diseases.

These paragraphs are preceded by the more important one which is:

(1) To promote the general welfare through the efficient control of injurious insects and plant diseases affecting all economic and ornamental plants and their products.

The Crop Protection Institute, therefore, is planned to in no way take the place of existing work, but to offer a common forum in which the manufacturers—that is the commercial interests—and the purely scientific interests may come together and discuss types of work, state of the work now in progress, and to plan research to fit into some particular niche.

In our organization, the affairs are in the hands of a board of nine scientific men; there may be more added if necessary. Three of these come from the Association of Economic Entomologists, three from the American Phytopathological Society, two from the Association of Official Agricultural Chemists and one from the National Research

Council. There have been no meetings of this board since your representatives were appointed. That is why I am making a brief report to you, supplementing theirs. I hope another year you can call upon them for a report of their activities, and that you will learn more of real progress than I am able to give you because we are going through the organization stage.

However, during this period of organization the institute has been useful. In the field of agriculture it offered its facilities for the presentation to the manufacturers of calcium arsenate advice by B. R. Coad, as to what is necessary if the program to control the boll weevil through the application of calcium arsenate is to be a success. That meeting, held in New York, was attended by manufacturers and chemists, and the subject was discussed from the standpoint of the entomologist, the chemist and the mechanical engineer. Questions of application including machinery, the things that were wrong and the things that were most efficient for the application of the dust, and the physical properties of calcium arsenate were fully discussed. Manufacturers, in the first instance, sent into the South much material that could not be used for the purpose; also there was not sufficient information as to the methods of application.

In this instance the Department of Agriculture did not wish to bring together officially the manufacturers of these poisons and the manufacturers of the dusting machinery. The institute was very glad to ask these people to come together under its auspices, which made it quite unofficial, and the entire program was given over to representatives of the Department of Agriculture who presented these various matters as well as the first showing of the film depicting the control of the boll weevil.

The Board of Governors of the institute hoped very much to have at this time rather interesting data on a cooperative experiment on dusting which it was planned to carry forward in Virginia, West Virginia, Pennsylvania, New York and New Jersey this year. We wished to get some real information on the efficiency of dusting, especially on apples, as compared with spraying, but in the spring the frosts, as you know, killed most of the fruit, so very little if anything could be done. Under the circumstances, there was no use dusting or spraying in these localities, so the time has been lost in that particular experiment. The Board has also been interested in trying to lay out certain lines of research which might be carried on in some of the existing laboratories and have, at this time, two things particularly in mind. One has been the study from the chemical standpoint of sulfur and sulfur compounds to try to throw light on the use of sulfur as an insecticide. The other is the effect of climate on the efficiency of sulfur so used.

I think there is little more I can tell you concerning the present status of the institute. There is to be another meeting of the Board of Governors in New York to discuss the work for the coming year and to try to lay out a new program. I want to emphasize, in closing, that the Crop Protection Institute is purely a cooperative effort in which you have a real interest and that it seeks to avoid duplication. Getting together for conferences, working out research programs, presenting the resulting data in readable form to those who ought to have it and assisting in any way possible in the suppression of injurious insects and plant diseases are some of our worthy aims.

W. F. Hand: Dr. Howe has certainly made us a very interesting address, and we are glad he could find time to come.

REPORT OF SECRETARY-TREASURER FROM

By C. L. Alsberg (Bureau of

RECEIPTS.

1920		
Nov. 12	Bank balance	$ 921.48
Nov. 15	Deposited	.13
	Dues from 14* Canadian and State institutions received too late for inclusion in 1920 report	65.00
	Dues for year 1921 from 38† State, Municipal and Canadian organizations	170.00
	2 subscriptions to *Journal* deposited in Treasurer's account in error	9.00
	Total receipts	$1,165.61

*Dues from one State deposited in *Journal* account.
†Dues from four organizations deposited in *Journal* account.

NOVEMBER 15, 1920 to JUNE 21, 1921.

Chemistry, Washington, D. C.).

DISBURSEMENTS.

1920				Amount	Check No.
Nov. 20	Telephone calls, car fare, New Willard Hotel			$ 1.95	4
Nov. 20	Tips, New Willard, 1920 meeting			32.00	5
	Bastian Bros. Co., badges 1920 meeting				
	252 at $ .21	$ 52.94			
	Postage	.51			
	Insurance	.25			
			53.70		
	Less 1% discount		.54		
				53.16	6
Dec. 20	The postmaster, Washington, D. C., box rent, quarter ending March 31, 1921			2.00	7
Dec. 20	Chas. G. Stott & Co., printing 5000 letter heads, 2 boxes thin second sheets			34.96	8
1921					
Feb. 10	Postage			5.00	9
Mar. 24	The postmaster, Washington, D. C., box rent, quarter ending June 30, 1921			2.00	10
Apr. 7	A. F. Humphreys, stenographic services reporting 1919 meeting			9.20	11
	Total disbursements			$ 140.27	
	Bank balance			1,025.34	
				$1,165.61	

REPORT OF SECRETARY-TREASURER FROM

By R. W. Balcom (Bureau of

RECEIPTS.

1921		
June 21	Bank balance	$1,025.34
	Dues from 14 Federal, State, Canadian and Municipal Organizations	95.00
	Total	$1,120.34

JUNE 21, 1921, TO OCTOBER 15, 1921.

Chemistry, Washington, D. C.).

DISBURSEMENTS.

1921			Amount	Check No.
Aug. 29	Cash for postage for mailing programs		$ 11.66	13
Sept. 22	Byron S. Adams for printing 1000 programs, 1921 meeting		37.50	14
Sept. 26	Industrial Printing Co., on account (*Journal*)		500.00	15
Oct. 13	Industrial Printing Co., on account (*Journal*)		200.00	16
Oct. 15	Bastian Bros. Co., 410 badges, 1921 meeting		72.03	17
Oct. 15	Bank balance	$ 371.18		
	Less Check No. 17 outstanding	72.03		
			299.15	
	Total		$1,120.34	

FINANCIAL REPORT ON PUBLICATIONS FROM

By C. L. Alsberg* (Bureau of Chemistry,

RECEIPTS.

1920				
Nov. 18	Bank balance			$ 1,890.44
	Total deposits		$ 10,262.82	
	Loss on exchange	$ 2.13		
	Less redeposited checks	100.00		
	Less check returned because of insufficient funds	5.00		
			107.13	
				10,155.69
				$12,046.13

DETAILED STATEMENTS RELATIVE TO RECEIPTS.

Journal Subscriptions.

No. ordered	Price each	Total cost	
14	$5.50	$ 77.00	
335	5.00	1,675.00	
13	4.40	57.20	
109	4.00	436.00	
55	3.75	206.25	
10	1.50	15.00	
10	1.40	14.00	
6	1.25	7.50	
Total		$ 2,487.95	
Less loss through exchange†		.93	
Total			$ 2,487.02

Methods Subscriptions.

No. ordered	Price each	Total cost		
49	$5.50	$ 269.50		
1394	5.00	6,970.00		
25	4.40	110.00		
70	4.00	280.00		
Total		$ 7,629.50		
Less loss through exchange†		1.83		
Total			$ 7,627.67	
Total, Journals and Methods				$ 10,114.69
Plus $16.00 returned because of excess payment		$ 16.00		
Plus bank balance		1,890.44		
Plus dues, 5 institutions		25.00		
				1,931.44
				$12,046.13

*Present address, Food Research Institute, Stanford University, Calif.
†Includes loss on exchange plus difference through over and under subscription.

NOVEMBER 18, 1920 TO JUNE 18, 1921.

Washington, D. C.), *Chairman, Board of Editors.*

DISBURSEMENTS.

1920		Amount	Check No.
Nov. 20	Postage, sending out Methods	$ 50.00	42
Nov. 23	Industrial Printing Co., on account	1,500.00	43
Nov. 26	N. A. Parkinson, freight and drayage on Methods	1.18	44
Nov. 27	Calif. Dept. of Agriculture, refund on excess payment on Journal	1.00	45
Dec. 8	Postage	25.00	46
Dec. 8	Frederick E. Everett, State House, Concord, N. H., refund for excess payment made on Book of Methods	5.00	47
Dec. 20	Industrial Printing Co., on account	1,000.00	48
1921			
Jan. 3	Western Union Telegraph Co., reimbursement telegram to Doolittle	.70	49
Jan. 4	Industrial Printing Co., on account	1,000.00	50
Jan. 4	Farran's Transfer and Storage, hauling Journals	1.00	51
Jan. 6	Postage, sending out Methods, etc.	50.00	52
Jan. 11	Industrial Printing Co., on account	1,000.00	53
Feb. 8	Postage	5.00	54
Feb. 8	U. S. Post Office, 5,000 S. R. 2c. envelopes	125.00	55
Feb. 10	Industrial Printing Co., on account	1,000.00	56
Feb. 10	Postage, sending out Methods	50.00	57
Feb. 15	Industrial Printing Co., on account	1,000.00	58
Mar. 10	Atlas Powder Co., Philadelphia, Pa., reimbursement for express charge on Book of Methods	.39	59
Mar. 12	Industrial Printing Co., on account	1,000.00	60
Mar. 14	Postage	25.00	61
Mar. 17	Cleveland Provision Co., reimbursement excess payment made on Book of Methods	15.00	62
Mar. 19	Herman Goldberger, overpayment on Journal	1.00	63
Mar. 23	Postage, sending out Journal circular letters	123.00	65
Mar. 24	Emanuel Baumgarten, rubber stamps	1.25	66
Mar. 24	Postage, sending out Methods	10.00	67
Apr. 7	Postage, sending out Methods	10.00	68
Apr. 21	Postage, sending out Methods	10.00	69
Apr. 26	N. A. Parkinson, expenses trip to Baltimore	6.10	70
Apr. 29	Postage, sending out Methods and Manuscripts	10.00	71
May 3	R. P. Andrews Paper Co., 500 clasp envelopes	7.08	72
May 9	N. A. Parkinson, reimbursement for drayage charges on Vol. IV, No. 3	1.00	74
May 9	Postage, sending out Vol. IV, No. 3 to foreign subscribers. Office postage	10.00	75
May 11	Industrial Printing Co., on account	1,000.00	76
May 11	Postage, sending out Journal & Methods circular letters	250.00	77
May 25	Postage, sending out Methods and Journals	10.00	78
May 28	N. A. Parkinson, reimbursement expressage charges on 100 copies Vol. IV, No. 1	1.06	79
June 2	Postage, sending out Methods and foreign Journals	10.00	80
June 18	Bank balance $2,732.53		
	Less check No. 29 outstanding 1.16	2,731.37	
		$12,046.13	

FINANCIAL REPORT ON PUBLICATIONS FROM

By R. W. BALCOM (Bureau of Chemistry,

RECEIPTS.

1921					
June 19	Bank balance				$ 2,731.37
	Total deposits		$ 2,861.83		
	Less check returned for discount	$ 4.00			
	Less redeposited checks	20.00			
	Less checks returned because of insufficient funds and improperly drawn	10.10			
			34.10		
					2,827.73
					$ 5,559.10

DETAILED STATEMENTS RELATIVE TO RECEIPTS.

Journal Subscriptions.

No. ordered	Price each	Total cost	
19	$5.50	$ 104.50	
134	5.00	670.00	
10	4.40	44.00	
5	4.20	21.00	
42	4.00	168.00	
28	3.75	105.00	
4	1.50	6.00	
4	1.25	5.00	
Total		$ 1,123.50	
Less loss through exchange		.67	
Total			$ 1,122.83

Methods Subscriptions.

No. ordered	Price each	Total cost		
7	$5.50	$ 38.50		
270	5.00	1,350.00		
11	4.40	48.40		
54	4.00	216.00		
Total		$ 1,652.90		
Less loss through exchange		.39		
Total			$ 1,652.51	
Total, Journals and Methods				$ 2,775.34
Plus checks returned because of excess payment		$ 52.39		
Plus bank balance		2,731.37		
				2,783.76
				$ 5,559.10

JUNE 19, 1921 TO OCTOBER 15, 1921.

Washington, D. C.), *Chairman, Board of Editors.*

DISBURSEMENTS.

1921			Amount	Check No
June 29	Postmaster, box rent and key deposit.		$ 2.20	82
June 29	Industrial Printing Co., on account.		2,000.00	83
June 29	N. A. Parkinson, office expenses		25.00	84
July 8	Industrial Printing Co., 2,880 wrappers for Journal; parcel post on 1,000		28.88	85
July 8	Industrial Printing Co., 1,000 cartons for Methods		26.00	86
July 11	F. W. Faxon Co., refund on subscription, Lewis Institute Library		3.00	87
July 12	American Railway Express, return of Book of Methods addressed to Leon Fisher		.46	88
July 18	Postmaster, deposit for mailing Journals at second-class mail rate		25.00	89
July 19	Dept. of Beverage Inspection, Jefferson City, Mo., refund on subscription		3.00	90
July 21	N. A. Parkinson, expenses trip to Baltimore		6.30	91
July 28	Industrial Printing Co., on account.		1,000.00	92
Aug. 5	N. A. Parkinson, office expenses		25.00	93
Aug. 5	G. E. Stechert & Co., refund on 3 subscriptions Vol. III, Nos. 2–4 included in 1920 report; refund on 3 subscriptions Vol. IV, for University of Illinois Library included in July report		21.00	94
Aug. 5	Puget Sound News Co., refund on subscription for Washington University Library		1.00	95
Aug. 9	Underwood & Underwood, glossy print of Dr. Wiley		5.00	96
Aug. 11	D. Van Nostrand Co., reimbursement excess payment Methods		8.00	97
Aug. 16	Postmaster, 5,000 special request envelopes		125.00	98
Aug. 22	Chas. G. Stott & Co., Inc., Printing 5,000 letter heads		25.50	99
Sept. 1	Postage, mailing Journals and Methods		25.00	100
Sept. 7	R. W. Balcom, reimbursement W. B. & A. Ry. bill of Sept. 3.		1.02	101
Sept. 1	Williams & Wilkins, sent in accordance with letter of Chivers & Sons, Ltd., England, dated Aug. 25		5.62	102
Aug. 25	N. A. Parkinson, expenses to Baltimore		6.20	103
Sept. 7	Colgate & Co., refund on Book of Methods and Vols. IV & V		15.00	105
Sept. 12	St. Andrews Biscuit Works, reimbursement excess payment Vol. IV		13.77	106
Sept. 20	G. S. Fraps, reimbursement excess payment Vol. V		1.00	107
Sept. 20	Postmaster, box rent to Dec. 31		2.00	108
Sept. 22	Maryland State Dept. of Health, refund excess payment on Journal		1.00	109
Sept. 22	Industrial Printing Co., 5,200 wrappers.		38.50	110
Sept. 22	Industrial Printing Co., on account.		1,000.00	111
Sept. 26	N. A. Parkinson, office expenses		25.00	112
Oct. 8	Industrial Printing Co., on account		500.00	113
Oct. 8	R. E. Rose, reimbursement for excess payment on Journal		1.00	114
Oct. 15	Industrial Printing Co., on account		423.02	115
Oct. 15	W. O. Emery, payment on back numbers of Journal purchased from him		8.00	116
Oct. 15	Bank balance	$ 593.65		
	Less outstanding checks	431.02		
			162.63	
			$5,559.10	

R. W. Balcom: In connection with the matter of the suit against the Williams and Wilkins Company there is a question whether the association wishes to take any further action in the matter. Briefly, the status of the case is as follows: Number 1 of Volume 3 of *The Journal* was the last number published by that company. Owing to some disagreement the publication was then suspended and was not resumed until November, 1919, when arrangements were made with another company to do the printing, merely as job work; that is, there was no contract except that they agreed to do such work as was given to them. They, of course, gave us an estimate as to how much it would cost. The former publishers had been handling the subscription list and receiving all the subscriptions to *The Journal.* Subscriptions are paid in advance, and therefore they received practically all the subscriptions to Volume 3 of *The Journal.* They published one number and we published the other three numbers of Volume 3. We felt it was our duty to supply the subscribers with the other numbers of Volume 3 as it was no fault of theirs that this trouble with the publishers occurred. Dr. Alsberg has felt that the Williams and Wilkins Company has about $4,000 of the association's money. The exact amount can not be ascertained unless we should sue for an auditing. They brought suit for damages to the extent of $50,000, that amount being based very largely upon future profits which they hoped, or at least pretended to hope, to get out of the contract. The question now for the association to decide is whether it wants to take any further action—that is, legal action—in this matter. I have tried to get a little legal advice in the last few days. Mr. Frank of the Baltimore office of the law firm representing the association advised by phone that although he was not quite sure that we were debarred by the statute of limitations from doing anything, he thought possibly that might stand in the way, but he would prepare a written statement.

That is about the status of the case. It is very problematical as to whether we should take any legal action. In the first place, we do not know how much money we are entitled to, and in the second place it would be costly to attempt to recover it. The association should take some action; if it feels that it has not enough information at present to decide whether it is advisable to bring a counter-suit or to dismiss the matter altogether it is suggested that the matter might be referred to the incoming executive committee with power to act in the matter because it would not be well to wait until next year. I am sure the chair will be glad to entertain any motion in the matter.

W. W. Skinner: What do you say the amount involved is?

R. W. Balcom: We do not know, but it is estimated between $4,000 and $6,000. Whether or not that estimate is anywhere near the truth

we can not find out unless we sue for an accounting and ascertain just how much we are entitled to. We would have to pay an expert accountant and his work would be difficult, without doubt, owing to the opposition of the company.

W. W. Skinner: What is the present status of the finances of the association?

R. W. Balcom: On October 15, considering all our resources, we had a deficit of about $950.

W. W. Skinner: Is there a prospect of liquidating that?

R. W. Balcom: A prospect of liquidating that if we do not get any money from the Williams and Wilkins Company? We hope to do that, but it remains to be seen.

L. F. Kebler: I do not know the exact relations and feelings that exist between this publishing company and this association. It just ran through my mind whether or not it would be possible with a new set of representatives of this association for one of these representatives to go to the company and talk the matter over in a general way, to see if a gentlemen's agreement can not be reached. You can frequently do more in that way than you can by litigation.

H. C. Lythgoe: I may say that my experience with that company has not been satisfactory. I had serious difficulty with them myself and our State Department did, too, in regard to our subscriptions. It would, no doubt, cost considerable to bring any suit against them and I would not care to have this association vote right out and out to bring suit, but I think the best thing to do would be to leave this matter with the executive committee with power to act.

W. W. Skinner: I do not believe it is good practice to send good money after bad money. I would move, therefore, that the matter be left with the new executive committee with the suggestion from the association that it probably would be inadvisable to bring suit.

L. F. Kebler: I second the motion. I do not think Mr. Lythgoe's experience with the company would preclude having a talk with the representatives of the company.

R. W. Balcom: I may say for the information of the members of the association that before I learned that the case had been dismissed I had already taken steps to see if it were possible to have an interview with the company to see how they felt about a compromise. Negotiations had been started toward that end when I learned that the case had been dismissed, but it would seem to me to be entirely practicable for some officer of the association to go to them if the association decides not to take any further legal action. It would not do to go while that question is still pending, but if our representative could tell them posi-

tively that the association considered the matter closed so far as any further legal action was concerned, then it might be possible to make them see that it would be to their interest to refund part of the money. They might not see it that way, but it would do no harm to have such a conference.

W. F. Hand: I hope that if a representative of the association has a conference with this company he will be successful in his negotiations.

H. A. Huston: I think that firm is also engaged in publishing a number of other associations' journals, and many of the men who support those journals are also members of this association. A little pressure might be brought to bear in that way.

W. F. Hand: Dr. Huston's suggestion is a good one. I think the present executive committee has already considered that point; we will refer it to the new committee.

The motion that the matter be left with the Executive Committee with the suggestion from the association that it probably would be inadvisable to bring suit was carried.

REPORT OF AUDITING COMMITTEE.

The auditing committee has made as thorough an examination of the reports of the secretary-treasurer and of the chairman of the Board of Editors as the limited time and their inexperience would permit and report that they are correct to the best of their knowledge and belief.

The committee believes that in view of the fact that the association does not have among its members persons with training along the lines of accountancy, in the future it would be a better procedure to have the treasurer's accounts audited by a public accountant, provided that this can be done without too great expense.

The committee, therefore, suggests that the treasurer be instructed to have his accounts audited by a public accountant prior to the 1922 meeting and submit the auditor's certificate with his report to the association.

Respectfully submitted,

J. J. T. Graham,
J. W. Kellogg.
Auditing Committee.

Adopted.

It was moved, seconded and carried that the suggestion of the Auditing Committee be referred to the Executive Committee with power to act.

REPORT OF COMMITTEE TO COOPERATE WITH OTHER COMMITTEES ON FOOD DEFINITIONS[1].

Your committee respectfully submits the following report of the proceedings of the Joint Committee on Food Definitions and Standards for the period since the 1920 meeting of this association.

The membership of the committee has been changed by the resignation of Carl L. Alsberg and the appointment by the Secretary of Agriculture of W. W. Skinner and R. E. Doolittle as the successors of Messrs. Alsberg and Abbott.

At its meeting last week, the Joint Committee elected William Frear to be chairman and A. S. Mitchell to be secretary.

During the past year the Secretary of Agriculture authorized and issued Food Inspection Decisions No. 181 (April, 1921) on cheese standards, and No. 182 (September, 1921) on citrus fruits, embodying the schedules of definitions and standards for these groups of commodities which had earlier been adopted by this association upon the recommendation of the Joint Committee.

The committee's activities for the period just closed have included meetings held in Washington, D. C., in November last and in March and October of the current year. Hearings were given in January on the subject of fruit pies; in March on the subject of potato flour; and in October on the subjects of bread and ginger ale.

At the March meeting, the Executive Committee of the Joint Committee made assignments for study of the following subjects:

Ice cream	Julius Hortvet
Dried and dehydrated fruits and vegetables	William Frear
Meat extracts	W. W. Randall
Non-alcoholic flavors	W. W. Skinner
Soy bean flour	C. D. Howard
Almond paste	C. D. Howard
Fruit juices	R. E. Rose
Extra-pharmacopœial drugs	L. E. Sayre.

The Joint Committee has finally adopted, after full publication to the food control officials of the nation and to the trade interests concerned—through the medium of the appropriate trade journals—and after careful weighing of all representations received as the result of such publication, the following schedule of definitions and standards, which it hereby submits with the recommendation that you approve the same:

CANNED CORN.

Definitions and standards adopted by the Joint Committee on Definitions and Standards, October 17, 1921:

Canned sweet corn, canned corn, is the canned vegetable properly prepared from the grain of sweet corn (*Zea mays* L.) of the proper degree of maturity, with or without the

[1] Presented by William Frear.

addition of sugar and salt, and with the addition of potable water sufficient to secure the consistency proper for the product.

CANNED SWEET CORN STYLES.

Cream canned corn is canned sweet corn prepared from corn removed from the cob by cutting through the grain and subsequent scraping. It has a creamy consistency.

Whole grain canned corn is canned sweet corn prepared from corn removed from the cob by cutting in such a manner as to leave the grain substantially entire.

CANNED SWEET CORN GRADES.

Fancy canned sweet corn is the product characterized by superior flavor and prepared from young, tender corn, the kernels of which are milky or creamy.

Extra standard canned sweet corn is the product characterized by good flavor and prepared from corn intermediate in tenderness between that used for the fancy and that for the standard grade.

Standard canned sweet corn is the product characterized by acceptable flavor and prepared from reasonably tender corn, the kernels of which have reached but not passed the dough state.

Substandard canned sweet corn is canned sweet corn which fails in some respect to meet the qualifications of standard grade.

CANNED TOMATOES.

Definitions and standards adopted by the Joint Committee on Definitions and Standards, October 18, 1921:

Canned tomatoes are the canned vegetables prepared from sound, ripe, fresh tomatoes (the fruits of *Lycopersicum esculentum* Mill.) of any red variety or varieties, by thorough washing and scalding and by proper peeling, coring and trimming, with or without grading, with or without the addition of sugar and salt, and properly sterilized by heat. The liquor used for filling the spaces between the fruits prior to sterilization, is the pure juice derived from the tomatoes so prepared or from others of the same quality and preparation, and does not exceed in quantity that necessary properly to process and protect the fruit.

CANNED TOMATO GRADES.

Fancy tomatoes are canned select tomatoes of uniform red color, free from pieces of skin or core, and are, at least for the most part, whole tomatoes, with or without a few almost whole tomatoes, and with or without a few large pieces.

Extra standard tomatoes are canned tomatoes practically free from under-colored parts and from pieces of skin or core. Most of the fruits are whole or in large pieces.

Standard tomatoes are canned tomatoes reasonably free from under-colored parts and from pieces of skin or core.

Substandard tomatoes conform to the definition for canned tomatoes but lack in some respect the qualifications of the higher grades.

FINAL DEFINITIONS AND STANDARDS FOR STRAINED TOMATOES AND TOMATO PASTE.

Definitions and standards adopted by the Joint Committee on Definitions and Standards, March 25, 1921:

Strained tomatoes is the product obtained by straining sound, ripe tomatoes, raw or cooked, through a screen that removes skins and seeds.

Tomato paste is strained tomatoes concentrated by evaporation, with or without the addition of salt, with or without the addition of basil leaf (*Ocimum basilicum* L.), with or without the addition of pure sodium carbonate or of sodium bicarbonate to neutralize a portion of the acidity, and contains not less than twenty per cent (20%) of tomato solids determined by drying in vacuo at 70°C.

Concentrated tomato paste is strained tomatoes concentrated by evaporation, with or without the addition of salt, with or without the addition of basil leaf, with or without the addition of pure sodium carbonate or of sodium bicarbonate to neutralize a portion of the acidity, and contains not less than thirty per cent (30%) of tomato solids determined by drying in vacuo at 70°C.

Strained tomatoes from trimming stock is the product obtained by straining sound peelings, trimmings and pieces from ripe tomatoes through a screen that removes skins and seeds.

Tomato paste from trimming stock is strained tomatoes from trimming stock concentrated by evaporation, with or without the addition of salt, with or without the addition of basil leaf, with or without the addition of pure sodium carbonate or of sodium bicarbonate to neutralize a portion of the acidity, and contains not less than twenty per cent (20%) of tomato solids determined by drying in vacuo at 70°C.

Concentrated tomato paste from trimming stock is strained tomatoes from trimming stock concentrated by evaporation, with or without the addition of salt, with or without the addition of basil leaf, with or without the addition of pure sodium carbonate or of sodium bicarbonate to neutralize a portion of the acidity, and contains not less than thirty per cent (30%) of tomato solids determined by drying in vacuo at 70°C.

Respectfully submitted,
William Frear,
Julius Hortvet,
Committee to Cooperate with other Committees on Food Definitions.

Adopted.

REPORT OF NOMINATING COMMITTEE[1].

The following names are respectfully submitted:

President, F. P. Veitch; *Vice-President*, A. J. Patten.
Executive committee: H. D. Haskins and R. E. Doolittle.
Board of Editors: R. B. Deemer.
Secretary-Treasurer, W. W. Skinner.

R. W. Balcom,
H. C. Lythgoe,
R. N. Brackett.
Nominating Committee.

William Frear: I move that the secretary of the association be directed to cast the ballot for the officers nominated.

The motion was seconded and carried.

[1] Presented by R. N. Brackett.

W. F. Hand: The secretary will cast the vote of the association for the officers named.

R. N. Brackett: The committee did not understand that this would remove Dr. Balcom from the Board of Editors.

R. W. Balcom: The action of the association has left the chairmanship of the Board of Editors to be filled by election.

R. N. Brackett: The Nominating Committee did not understand that that removed Dr. Balcom from the position. If it is the sense of the association, I am sure that every member of the committee was favorable to Dr. Balcom being retained as chairman of that committee. If you want to make it official I will cast the vote over again.

W. F. Hand: We will make it by unanimous consent.

R. N. Brackett: While I am on my feet I want to make a resolution. In view of the long service rendered to this association by one of its members who is no longer with us, a service characterized by faithfulness and exceptional efficiency, during which time he served as secretary of the association, and in view of his efforts in the successful organization and establishment of our *Journal*, a task beset with many difficulties and requiring more than ordinary ability and tact—and I might even add that this gentleman shouldered personally the financial responsibility for the project at one stage of procedure—and in view also of the active part which he took in the restoration of cooperation between the States and the Federal Department in the matter of food definitions and standards,

Therefore be it resolved, That Dr. Carl L. Alsberg be elected an honorary life member of this association. By so doing we shall not only recognize ability and efficiency, but honor ourselves in honoring him.

The resolution was seconded and carried by a rising vote.

REPORT OF COMMITTEE ON RESOLUTIONS[1].

The association has, since its last meeting, lost one member by death, Professor Bert Holmes Hite. Your committee recommends the adoption of the following resolution:

Resolved, That by the death of Professor Bert Holmes Hite, Chief Chemist of the West Virginia Agricultural Experiment Station, this association has lost a distinguished member, one who has rendered long and valuable service to his commonwealth, and whose researches have produced valuable contributions to chemical knowledge.

Resolved, That the secretary of the association transmit copies of this resolution to the West Virginia Agricultural Experiment Station and to Professor Hite's family.

[1] Presented by William Frear.

Resolved, That the Association of Official Agricultural Chemists hereby expresses to the Secretary of Agriculture its appreciation of his high estimate of the service which is being rendered to the country by its members and their fellow chemists, and of his tender of cooperation.

Resolved, That this association hereby expresses to its president, W. F. Hand, its thanks for the courteous, efficient manner in which he has conducted the proceedings of the present convention.

Resolved, That this association hereby expresses to Miss Nellie A. Parkinson its sincere appreciation of her efficient work relating to *The Journal* of the association and of the services she has rendered in making this convention a success.

Resolved, That the thanks of this association be tendered to the management of the Hotel Washington for the facilities provided and the courtesies extended to the association and its members.

Resolved, That this association endorses the proposal now under consideration by Congress that, after due notice, the metric system of weights and measures be made the legal system of the United States; and also, to further the introduction of this system, recommends that its members, in the purchase of supplies, designate and describe the same in terms of the metric system so far as possible.

Whereas, The agricultural and other industrial interests of the country realize the necessity of a trained chemical personnel and the advantages arising from the application of chemical research to all industrial problems; and

Whereas, The research necessary for the solution of agricultural and other industrial problems can only be carried on with the aid of a firmly established chemical industry; and

Whereas, The development of chemical industry is one of the great factors tending toward the future welfare of our country, whether in times of peace or in times of war, it is therefore

Resolved, That the Congress of the United States is hereby urged to continue adequate, beneficial legislation until the various chemical industries in the United States have become firmly established; and

Whereas, The members of this association are engaged in the study and development of investigational methods as applied to agricultural and other industrial sciences, all looking toward the ultimate welfare of our country; and

Whereas, Our association earnestly advocates the promotion of peaceful industries and cordial relationships among scientific men throughout the world; be it therefore

Resolved, That this association expresses its hearty endorsement of the aims and purposes of the Conference on the Limitation of Armaments to be held in this city beginning November 11; and be it further

Resolved, That it is the hope of the Association of Official Agricultural Chemists in convention assembled, that the highest aims and purposes of the Conference on the Limitation of Armaments may be attained, thereby realizing the hopes of the American people and of humanity at large.

Resolved, That the secretary of this association do and is hereby instructed to send copies of these resolutions to the chairmen of the Congressional Committees convened and to the proper Executive officers.

Adopted.

BERT HOLMES HITE

On October 6, 1921, occurred the death of Professor Bert Holmes Hite, chemist and vice-director of the West Virginia Experiment Station. Professor Hite was born in 1866, received the degree of Master of Science from the University of West Virginia in 1890 and attended Johns Hopkins University from 1891 to 1895, being a fellow from 1893 to 1895. He was appointed Chief Chemist in the Experiment Station in 1895, Professor of Organic Chemistry in the University of West Virginia in 1896, and was made Agricultural Chemist of the State in 1898 and Vice-Director in the Experiment Station in 1902. He was also made chief chemist of the West Virginia Geological Survey in 1898 and served as consulting chemist of the Baltimore and Ohio Railroad, 1916 to 1918. During 1918 he did research work for the Ordnance Department of the Army. He was a member of the American Chemical Society, the Electrochemical Society and the Franklin Institute.

Professor Hite was an untiring worker, and it was seldom that he could not be found late at night in his laboratory. Because of his dislike for public attention but few, even of his own townsmen, knew of his achievements, but he was an expert on molecular weights, combustion, soils, and high-pressure researches and in bacteriology. For notable achievement in his high-pressure work the Franklin Institute recently conferred upon him a medal for research.

Professor Hite was unusually thoughtful and courteous in his dealings with his associates, and his fine qualities of character endeared him to all who knew him well.

His death occurred at Johns Hopkins Hospital, Baltimore, from a cancerous condition of the spine.

H. H. HANSON.

The Convention adjourned.

CONTRIBUTED PAPERS.

METHODS FOR THE ESTIMATION OF SMALL AMOUNTS OF STARCH IN PLANT TISSUES.

By F. E. Denny[1] (Bureau of Chemistry, Laboratory of Fruit and Vegetable Chemistry, Los Angeles, Calif.).

While studying the changes in the composition of cantaloupes during the ripening period in this laboratory, in following out a suggestion made by C. L. Alsberg, it was noted that the development of maturity in melons was accompanied by a decided reduction in the starch content of the seeds.

Thus, while seed extracts from immature melons always gave a strong positive test for starch by the iodine method, similar extracts from the seeds of ripe melons generally gave either a weak test, or one which indicated the complete absence of starch. It was desired to measure this progressive change quantitatively, in order to determine what correlation existed between the stage of maturity of a melon and the starch content of its seeds.

Cantaloupe seed powders, however, were found to contain only small amounts of starch. Preliminary tests with ordinary starch methods indicated that the starch contents were low, but a dependable estimate could not be obtained by their use. It is now known that even very immature melons have less than 2 per cent of starch in the seeds, that most of the seed samples used in this investigation contained less than 1 per cent of starch, and that ripe samples contained less than 0.2 per cent.

A method was needed that would cover the range from 0 to about 1 per cent of starch by steps of about 0.1 per cent. The methods here described, applied to cantaloupe seed powders, fulfilled this condition in a satisfactory manner. Since they seem to be open to further improvement and to offer the possibility of application to other kinds of material, they will be described in detail.

APPLICABILITY OF DIFFERENT STARCH METHODS TO CANTALOUPE SEEDS.

The official acid hydrolysis method[2] proved to be entirely unsuitable, as a certain seed sample showing only a trace of starch by qualitative test indicated a starch content of 2.30 per cent by this method, while the result with another lot giving a strong starch test was 2.26 per cent.

---

[1] The advice and helpful suggestions given by E. M. Chace, under whose direction this work was done, are acknowledged, as well as the cooperation of C. G. Church in working out the details of the methods.

[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 95.

Thus the method not only failed to distinguish between the two lots, but also gave for both starch values that are known to be too high.

A modification of the official diastase method[1], using taka-diastase instead of malt diastase, was also undependable. The results did not agree with the qualitative starch-iodide tests. Samples known to contain starch required no more permanganate for titrating[1] than did the blank, and samples containing traces of starch gave starch values known to be too high.

Attention was then directed to the starch method proposed by Von Fellenberg[2]. By this method the starch is dissolved in concentrated calcium chloride solution, precipitated as starch-iodide, the iodine dissolved and the starch precipitated by alcohol. The starch precipitate is then filtered, dried, weighed, ignited, reweighed and the difference taken as starch. The amounts of starch obtainable for weighing by this method were too small in the case of cantaloupe seed powders to give sufficiently accurate results. As that portion of Von Fellenberg's method which involved dissolving the starch in calcium chloride solution, however, was well suited to this material, it was adopted in applying the following methods.

Further progress was made by employing modifications of the method described by Long[3]. According to this method, a measured amount of the starch solution of unknown concentration is pipetted into a volumetric flask, together with some potassium iodide solution. A measured amount of standardized iodine solution is then added, the starch precipitated as starch-iodide, which is filtered off, and washed with potassium-iodide solution, and the iodine in the filtrate titrated with standard sodium thiosulfate. The values so obtained are compared with similar values by using starch solutions of known concentration.

In attempting to apply this method to cantaloupe seed extracts, serious difficulties were encountered. In the first place, even after extraction with fat solvents, substances other than starch, that in some manner remove iodine from solution, are present in these seed extracts. Furthermore, the calcium chloride itself contained substances that absorbed iodine.

These difficulties were overcome by two modifications of Long's method: First, by reversing the procedure and titrating the iodine in the starch-iodide precipitate, using the absorbed iodine rather than the residual iodine as a measure of the starch; second, by successively reprecipitating the starch-iodide, thus obtaining a partially purified starch solution to which the Long method could be applied.

Attempts were made, after separating the starch as starch-iodide, to hydrolyze the starch by acid and obtain a measure of the starch by the

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 80.
[2] *Mitt. Lebensm. Hyg.*, 1916, 7: 369.
[3] *Trans. Kan. Acad. Sci.*, 1916–1917, 28: 172.

reducing power of the dextrose formed. A small amount of starch was obtainable in this way from seeds of low starch content, so that the reduction produced in Fehling's solution required little permanganate for titration[1]. This difficulty, however, was overcome by a modification of Scales' method[2] which required relatively large amounts of thiosulfate for the titration of small quantities of dextrose.

PREPARATION OF SEED POWDER AND EXTRACTION OF STARCH WITH CALCIUM CHLORIDE.

The seeds were first ground coarsely, extracted with petroleum ether at room temperature and dried in an oven at 100°C. The residue was then in condition to be reduced to a fine powder by being ground in a mill until all the particles would pass through a 30-mesh sieve. The mill used was not capable of producing a finer powder with this material.

From this oven-dry powder, samples (usually 10 grams) were weighed out and put in 400 cc. beakers, 15 cc. of water were added and the mixture was stirred until the particles were wet. One hundred cc. of a saturated solution of calcium chloride were added; the mixture was slowly raised to the boiling point with occasional stirring, and gentle boiling continued for 15 minutes. Then 100 cc. of boiling water were added, and after thorough stirring the hot liquid was filtered through paper into a volumetric flask (usually 250 cc.). Most of the residue was retained in the beaker and was extracted successively with small portions of half-saturated calcium chloride. On cooling, the final volume was made up to the mark. The seed extract so obtained is clear, forms no precipitate on standing and is comparatively stable.

GENERAL DESCRIPTION OF STARCH METHODS USED.

After the starch was obtained in calcium chloride solution, the following methods were used for its quantitative estimation:

(1) By removing an aliquot, precipitating the starch as starch iodide under a standardized set of conditions and titrating the iodine in the starch iodide with standard sodium thiosulfate. Values so obtained were then compared with those given by known amounts of starch under the same conditions. The method will hereafter be referred to as the absorbed-iodine method.

(2) By removing an aliquot, precipitating the starch with iodine, purifying the starch-iodide by successive reprecipitations, regenerating a starch solution by the removal of the iodine with thiosulfate, again precipitating the starch as starch-iodide under standardized conditions and titrating the residual iodine. This will hereafter be referred to as the residual-iodine method.

(3) By removing an aliquot, precipitating the starch with iodine, hydrolyzing the starch with acid and estimating the dextrose formed by the official method[1] and that of F. M. Scales[2]. This method will be referred to hereafter as the reduction method.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 80.
[2] *J. Ind. Eng. Chem.*, 1919, 11: 747.

Most of the experimental work here reported was done in connection with the first method, only limited observations being made upon the other two.

DETAILS OF THE ABSORBED-IODINE METHOD.

Inasmuch as the ability to obtain consistent results with this method was closely connected with the technique of obtaining the starch-iodide precipitate and estimating its iodine content, the procedure used will be described in detail, as follows:

An aliquot was first pipetted into a centrifuge bottle, the amount taken varying from 100 to 400 cc., depending upon the starch content. A preliminary qualitative test by iodine in comparison with standard solutions of known starch concentration was sufficient to indicate approximately the amount to be used.

To the liquid in the centrifuge bottle, strong iodine solution (about 0.1N) was added drop by drop, until a blue color remained on standing several minutes, the object being to satisfy approximately the non-starch iodine-absorbing substances present. Then for each 100 cc. aliquot, exactly 20 cc. of 0.02N iodine solution were added, the bottle was shaken and the mixture allowed to stand (usually overnight). The iodine added must be in a sufficient excess (otherwise precipitation will not be produced) and it must be exactly the same amount and of the same concentration as that added to the standard starch solutions used for comparison. If the iodine added is insufficient to bring about precipitation, a smaller aliquot must be taken and made up to 100 cc. with half-saturated calcium chloride solution before the addition of iodine.

The starch-iodide precipitate is thrown to the bottom of the bottle by centrifuging and the liquor above drawn off. A glass tube drawn to a coarse capillary and connected with a suction flask is convenient for this purpose and allows the removal of the liquor without disturbing the precipitate.

Two difficulties were encountered at this point. In a few samples precipitation did not take place under these conditions. Such samples were rejected. Usually precipitation could be brought about by diluting with water and adding more iodine, but this operation causes a deviation from the standardized procedure. If data from such samples are required, it can be obtained by separating the precipitate obtained in this way, removing the iodine by the addition of exactly enough thiosulfate, again dissolving in calcium chloride solution, and following the standardized procedure. The cantaloupe seed extracts, however, almost always gave sufficiently good precipitation.

A second difficulty results from the fact that in practically no case is the precipitation absolutely complete. Very fine particles remain suspended in the liquid. These constitute only a small percentage of the total precipitate, however, and it is believed that the error involved in neglecting them is small. To remove them by filtration and return them to the main precipitate was not found to be feasible.

The starch-iodide precipitate was transferred to a hardened filter (12½ cm.) by means of 25 cc. of potassium iodide solution, containing 10 grams per 100 cc., and this precipitate washed with 75 cc. of potassium iodide solution, containing 5 grams per 100 cc. These solutions serve the double purpose of removing the excess iodine and at the same time holding the starch-iodide in precipitation. (The excess iodine is not completely removed by the process, and it was impracticable to bring about complete removal. Since the procedure is a standardized one, however, it permits a comparison of the seed extract precipitate with that of a known starch solution treated in the same way.) After filtration was complete, the bottom of the filter paper was punctured and most of the starch-iodide washed into a 400 cc. beaker with a jet of water, after which the filter paper with the remaining starch-iodide was added.

The problem now is to determine the amount of iodine present. This cannot be done by direct addition of thiosulfate, as the starch-iodide flakes do not break up readily and the end-point is not distinct. But if a measured excess of sodium thiosulfate is added and the mixture heated, the starch-iodide precipitate is broken up and the liberated iodine at once unites with the thiosulfate. The back titration with iodine is then a measure of the iodine content of the starch iodide, the starch acting as its own indicator. For these titrations, iodine and sodium thiosulfate of 0.005N strength were found to be most suitable, one or two drops giving a good end-point. Five to 15 cc. of thiosulfate were sufficient to give an excess, and the back titrations varied from none to about 10 cc. of iodine for the aliquots taken.

A list of titration values obtained by measuring the iodine absorbed by the starch in the seed extracts may be secured by this procedure. Such values are then compared with values obtained by treating starch solutions of known concentrations in a similar manner.

TABLE 1.

Iodine values of standard starch solutions.

STANDARD NO.	ALIQUOT TAKEN	STARCH TAKEN		IODINE FOUND		RATIO: Grams Iodine / Grams Starch
		Solution Concentration	Gram	0.005N	Gram	
	cc.	*gram per 100 cc.*		*cc.*		
A1	100	0.05	0.05	9.0	0.0057	0.11
2	100	0.05	0.05	9.0	0.0057	0.11
3	100	0.05	0.05	9.2	0.0058	0.12
4	100	0.05	0.05	8.8	0.0056	0.11
5	100	0.05	0.05	8.7	0.0055	0.11
6	100	0.05	0.05	9.1	0.0058	0.12
7	100	0.05	0.05	8.9	0.0057	0.11
B1	100	0.04	0.04	7.3	0.0046	0.12
2	100	0.04	0.04	7.1	0.0045	0.11
3	100	0.04	0.04	7.2	0.0046	0.12
4	100	0.04	0.04	7.2	0.0046	0.12
C1	100	0.03	0.03	5.3	0.0034	0.11
2	100	0.03	0.03	5.3	0.0034	0.11
3	100	0.03	0.03	5.2	0.0033	0.11
4	150	0.03	0.045	8.2	0.0052	0.12
D1	100	0.02	0.02	3.0	0.0019	0.10
2	100	0.02	0.02	3.0	0.0019	0.10
3	100	0.02	0.02	3.1	0.0020	0.10
4	150	0.02	0.03	5.4	0.0035	0.12
5	200	0.02	0.04	7.0	0.0044	0.11
6	200	0.02	0.04	6.5	0.0041	0.10
E1	200	0.01	0.02	3.6	0.0023	0.12
2	200	0.01	0.02	3.6	0.0023	0.12
3	150	0.01	0.015	2.5	0.0016	0.11
4	400	0.01	0.04	7.2	0.0046	0.12
F1	400	0.0075	0.03	4.6	0.0029	0.10
2	400	0.0075	0.03	4.7	0.0030	0.10
G1	200	0.0050	0.01	1.3	0.0008	0.08
2	200	0.0050	0.01	1.4	0.0009	0.09
3	200	0.0050	0.01	1.4	0.0009	0.09
4	200	0.0050	0.01	1.3	0.0008	0.08
5	400	0.0050	0.02	2.8	0.0018	0.09
6	400	0.0050	0.02	2.9	0.0018	0.09
H1	400	0.0025	0.01	1.1	0.0007	0.07
2	400	0.0025	0.01	1.2	0.0008	0.08

IODINE VALUES OF STANDARD STARCH SOLUTIONS.

Pure cantaloupe starch would have been preferable for standards of comparison. This tissue, however, contains such small amounts of starch and the grains are so minute that it would be impossible to obtain a sufficient quantity in the required state of purity. Since it was necessary to use another form of starch, potato starch was selected. A quantity of purified potato starch, whose purity was found by test to be 96.83 per cent, was obtained.

Starch was weighed out to make a solution containing 0.05 gram per 100 cc. when dissolved in calcium chloride in a manner similar to the procedure previously described. From this solution as a base, dilutions were made to produce the concentrations shown in Table 1, Column 3, the starch in each case being in half-saturated calcium chloride solution.

The solutions so obtained were slightly opalescent but transparent. They stood for weeks without the formation of a precipitate, although small particles which did not completely dissolve were noted. The question of the completeness of the solubility of the starch in calcium chloride is not important here, however, inasmuch as the aliquot taken in each represented a certain proportion of the original starch, and therefore could be directly compared with an unknown sample under the same conditions.

TABLE 2.

Average value of starch-iodine ratio.

ALIQUOT TAKEN	STARCH IN SOLUTION	IODINE REQUIRED	STARCH-IODINE RATIO
	gram per 100 cc.	*cc.*	
100	0.05	9.0	0.11
100	0.04	7.2	0.12
100	0.03	5.25	0.11
150	0.03	8.2	0.12
100	0.02	3.0	0.10
150	0.02	5.4	0.12
200	0.02	6.8	0.11
200	0.01	3.6	0.12
150	0.01	2.5	0.11
400	0.01	7.2	0.12
400	0.0075	4.65	0.10
			Average . . 0.11

From such standard solutions aliquots were taken and treated by the procedure already described for the seed extracts. The titration values, expressed in cubic centimeters of iodine corresponding to different aliquots of different starch standards, are shown in Table 1, Column 5, and the ratios of the iodine absorbed to the starch used are shown in

the last column. Table 2 is a summary of the data in Table 1 for the standards A to F, inclusive. Standards G and H had starch iodide precipitates too small in volume and deviated too far from the condition of proportionality between the starch taken and the iodine absorbed.

Attention is further directed to Fig. 1 in which the results are shown graphically. The black lines are lines of proportionality between the iodine and starch and correspond to the ratio 0.11, i. e., $\frac{\text{grams iodine}}{\text{grams starch}} = 0.11$. Backward extension of all the black lines will be found to pass through the origin. The crosses represent the average values obtained from Table 1 and show to what extent the values found correspond with the average ratio found in Table 2.

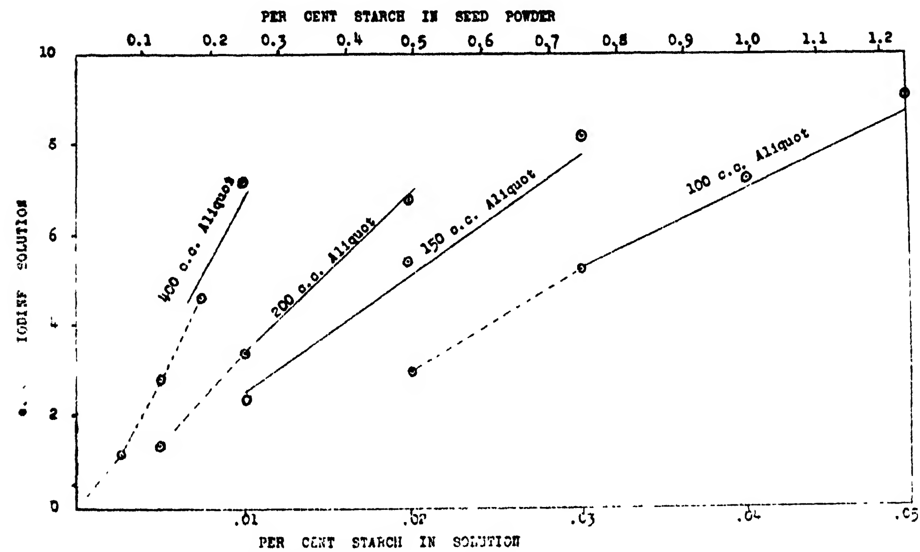


FIG. 1—VARIATION IN RELATION OF STARCH TAKEN AND IODINE ABSORBED.

Examination of the data in Table 1 and of the graph in Fig. 1 shows that strict proportionality between the iodine absorbed and starch taken was not found. Generally the ratio is high for the higher concentrations and low for the lower concentrations. This fact is no doubt connected with the volume of the starch iodide produced. Thus when the quantity of starch iodide is too low, too much iodine is removed by the washing process; and for the large amounts of starch-iodide, relatively too much iodine is retained.

It will be noted, however, that within narrow ranges the ratio is approximately constant, e. g., from 0.03 to 0.05 per cent for the 100 cc. aliquot, and from 0.01 to 0.03 per cent for the 150 cc. aliquot, etc. It is

interesting further to note that while the 100 cc. aliquot of 0.02 per cent starch solution falls below the line of proportionality, it is probably not caused by experimental error as may be seen from the agreement of duplicates for it in Table 1.

In applying the data from results on cantaloupe seed extracts, titration values that fell upon the black lines were converted into weights of starch by substitution in the equation $\frac{\text{grams iodine}}{\text{grams starch}} = 0.11$. For titration values falling upon the dotted lines, however, calculations were made by interpolation on the graph, the percentage of starch in solution being read from the bottom scale and the percentage of starch in the seed powder from the top scale. The percentage of starch in the seed powder was calculated on the following basis: 100 cc. of the seed extract correspond to 4.0 grams of seed powder.

VALUE OF THE STARCH-IODINE RATIO.

The value of this starch-iodine ratio, 0.11, may now be compared with that found by others. Taking a typical case from the results reported by Andrews and Goettsch[1], 8.08 grams of starch united with 0.518 gram of iodine, a ratio of 0.064[2]. Mellanby[3] carefully determined the point at which iodine and starch could be added in such proportions that neither starch nor iodine would appear in the filtrate. In a typical case, 0.087 gram of starch took up 0.0068 gram of iodine, giving a ratio of 0.078[4]. Long found that 0.00125 gram of starch removed 0.000254 gram of iodine, a ratio of 0.203[4]. It is pointed out by Mellanby, however, that two reactions are involved here: First, a quantitative one in which starch reacts chemically with iodine, forming a definite chemical compound; and second, "that the starch-iodide thus formed is a lyophobic suspensoid colloid, which adsorbs iodine from solution according to the recognized laws of adsorption".

Therefore the quantity of iodine taken up by a given amount of starch depends upon the concentration of the iodine with which it is in contact. When an excess of iodine is present, an additional amount will be adsorbed by the starch iodide precipitate. In all the experiments here reported, an excess of iodine was present (in fact, necessarily so, in order to produce precipitation), and an excess of iodine was always present in the starch-iodide precipitate. Hence values higher than Mellanby's for the ratios would be expected. The conditions in these experiments differed from those of Mellanby, in two other respects, namely, (1) much more dilute starch solutions were used, and (2) the starch was in solution, not in water but in half-saturated calcium chloride.

[1] *J. Amer. Chem. Soc.*, 1902, 24: 865.
[2] Calculations were made by the author.
[3] *Biochem. J.*, 1919, 13: 28.
[4] Calculations were made by the author.

DUPLICATE DETERMINATIONS ON SEED POWDERS BY THE ABSORBED-IODINE METHOD.

Duplicate samples of 10 grams were weighed out from cantaloupe seed powders. They were selected to exhibit the range of starch concentration found in this material. Thus, Lot No. 442 shows starch percentages at the upper limits; Lot No. 413B was a seed powder of low starch content and Lot No. 453 was intermediate in its starch content.

Each sample was carried through the procedure described, and the results show the sum of all of the errors of the process. (See Table 3.) Thus the titration values for 413B varied from 4.7 to 6.1, and the percentage of starch in seed powder calculated from the iodine titrations varied from 0.33 to 0.43. For Lot No. 453 these values varied from 5.5 to 6.6 and from 0.52 to 0.62, respectively.

TABLE 3.

Duplicate determinations on seed powders by the absorbed-iodine method.

LOT NO.	ALIQUOT TAKEN	IODINE TITRATION	STARCH FOUND	
			In Solution	In Seed Powder
	cc.	cc.	gram per 100 cc	per cent
442	100	8.3	0.047	1.18
442	100	7.8	0.044	1.10
442	100	7.9	0.045	1.20
442	100	7.7	0.043	1.08
	Average .	7.9	0.045	1.14
413A	200	8.4	0.048	0.60
413A	200	7.8	0.044	0.55
	Average .	8.1	0.046	0.58
413B	200	4.9	0.014	0.35
413B	200	4.7	0.013	0.33
413B	200	5.0	0.014	0.35
413B	200	6.1	0.017	0.43
413B	200	5.5	0.016	0.39
413B	200	5.0	0.014	0.35
	Average . . .	5.2	0.015	0.37
453	150	6.4	0.024	0.60
453	150	5.5	0.021	0.52
453	150	6.1	0.023	0.58
453	150	6.6	0.025	0.62
453	150	6.5	0.025	0.61
453	150	6.3	0.024	0.59
453	150	6.4	0.024	0.60
453	150	6.2	0.024	0.58
453	150	6.1	0.023	0.58
453	150	6.0	0.023	0.57
	Average . . .	6.2	0.024	0.58

A consideration of the data in Table 3 permits a rough approximation, at least, of the errors involved. Since the calculations are based on the iodine titration values, the variations in these values are the ones to be considered. The average iodine value for Lot No. 453 is 6.2; the probable error of a single observation is 0.2; the probable error of the mean of 10 observations is 0.06 and the probable error of the mean of two observations is 0.14. Hence the percentage error in using a single sample is $\frac{100 \times 0.2}{6.2}$, or about 3.3 per cent, and if duplicate samples were taken the error would be $\frac{100 \times 0.14}{6.2}$, or 2.3 per cent. If the average starch content of the sample is 0.58 per cent, the error of a single sample, expressed in percentage of starch in seed powder, is 3.3 per cent of 0.58 per cent, or 0.02 per cent, giving an error of 2 in the second decimal place.

In considering the results from Lot No. 413B, if the objection is made that the number of samples is too small to justify the calculation of the probable error, at least the average deviation of a single sample—which in this case is 0.4—may be determined. The percentage error of a single observation is thus found to be $\frac{100 \times 0.4}{5.2}$, or 7.7 per cent. Seven and seven-tenths per cent of 0.37 is 0.03, giving an error of 3 in the second place when the results are expressed in the percentage of starch in the seed powder. Considering the results of Lot No. 442 in the same manner, the percentage error of a single sample is 2.5 per cent, giving an error of 3 in the second place on the basis of the percentage of starch in the seed powder[1].

Many more such duplicate determinations would be necessary to obtain an accurate idea of the amount of the error involved in the method. In the work with cantaloupe seed powders, the results were thought to be sufficiently accurate to permit the expression of the starch content to the nearest 0.1 per cent.

ESTIMATION OF ADDED STARCH.

To weighed amounts of seed powder, weighed amounts of starch were added. The two samples (seed powder plus starch, and seed powder only) were carried through the process, and the iodine value of the check subtracted from that of the lot containing added starch. The amount of starch corresponding to the excess iodine was then calculated and compared with the weight of starch added. The results are shown in Table 4. Favorable results were found in Lots I, II and V, and unfavorable results in III and IV. But it may be pointed out that the quantity of starch used was small (particularly in Lot IV), in which case an error of a small amount of starch gives a large percentage error. The results in Table 4 seem to justify the belief that about 85–95 per cent of the added starch is recoverable in this way.

[1] A further error not taken into account here results from uncertainty as to the accuracy of the starch-iodine factor, 0.11.

TABLE 4.
Estimation of added starch.

	EXPERIMENT NUMBER				
	I	II	III	IV	V
Starch added to seed powder, grams...	0.1225	0.0770	0.0640	0.0174	0.0986
Volume of solution and aliquot taken..	500–150	250–100	250–150	250–100	250–100
Iodine titration (excess of total above seed powder alone) cc. 0.005N ...	6.1	5.0	5.6	1.5	6.6
Starch equivalent in aliquot taken, grams	0.035	0.029	0.032	0.009	0.038
Total starch found, grams.......	0.117	0.072	0.053	0.023	0.095
Percentage of added starch found ..	95	94	83	132	97

COMPARISON OF DIASTASE AND ABSORBED-IODINE METHODS ON CANTALOUPE SEED POWDERS.

Three seed powder lots containing percentages of starch among the highest found for cantaloupe seeds and one seed powder containing only a trace of starch were treated by both the diastase method[1] and the absorbed-iodine method. The following procedure was used for the diastase method:

Two duplicate lots of seed powder were taken; the first was gelatinized in boiling water and taka-diastase added. After the enzyme action had proceeded for 36 hours at 35°C., the liquid was filtered off, an aliquot hydrolyzed and the reducing power of an aliquot of this determined. The value so obtained is given under the heading "total reduction of aliquot" in Table 5. The duplicate lot of seed powder was treated exactly in the same way except that no taka-diastase was added, and the seed powder was not gelatinized but merely allowed to remain in water at 35°C., when it was filtered and an aliquot hydrolyzed as before. The value thus obtained is given under the heading "reduction due to non-starch substances" in Table 5. In addition, a sample of diastase solution equal in amount to that used with the seed powder was carried through the process in order to make the proper correction. Thus, in Table 5 the item "reduction due to starch only" is obtained by subtracting the reduction due to diastase alone and reduction due to non-starch substances from the total reduction. The dextrose value of the permanganate solution was obtained by titration against known concentrations of pure dextrose, and starch calculated from dextrose by the factor 0.9.

The percentages of starch found by the diastase method are shown in Table 5, and with them for comparison the results given by the absorbed-iodine method on the same powders. Although the agreement is not very satisfactory, more confidence is placed in the values given by the absorbed-iodine method than in those by the diastase method.

Thus, in Lot IV, the result with the diastase method seems too high, inasmuch as a qualitative test indicated only a trace of starch, while an iodine test on a starch standard of the indicated concentration gave a much stronger color. Additional evidence is found by comparing the diastase results of Lots III and IV. The starch content of the tissue in

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 95; 80, par. 29.

TABLE 5.

Comparison of diastase and absorbed-iodine methods.

TREATMENT OF POWDER BY DIASTASE METHOD	LOT NUMBER			
	I	II	III	IV
Seed powder taken, grams	5.0	6.2	5.0	7.0
Total reduction of aliquot, cc. $KMnO_4$	6.8	7.8	6.4	4.8
Reduction due to non-starch substances, cc. $KMnO_4$	3.5	1.9	0.2	0.1
Reduction due to diastase alone, cc. $KMnO_4$	1.7	3.4	3.4	3.6
Reduction due to starch only, cc. $KMnO_4$	1.6	2.5	2.8	1.1
Dextrose in aliquot, grams	0.0082	0.01285	0.0144	0.00565
Starch in aliquot, grams	0.0074	0.0115	0.0129	0.00500
Starch in entire sample, grams	0.0555	0.0867	0.0981	0.0375
Percentage of starch by diastase method	1.11	1.40	1.96	0.54
Percentage of starch by absorbed-iodine method	1.88	1.45	1.40	0.15

Lot III ranked among the highest of the samples analyzed, while that of the tissues in Lot IV was among the lowest. Yet the difference between them is represented by only 1.7 cc. of potassium permanganate. The difference between two such extremes could not be accurately separated into graded steps by the diastase method.

COMPARISON OF DIASTASE AND ABSORBED-IODINE METHODS ON OCA TISSUE (Oxalis tuberosa).

At the time of these experiments, the amount of starch in oca tissue was being estimated in this laboratory by a modified official diastase method, using taka-diastase instead of malt diastase, and some samples of this tissue were taken for comparison by the absorbed-iodine method. The results are given in Table 6.

TABLE 6.

Comparison of diastase and absorbed-iodine methods on oca tissue.

	EXPERIMENT NUMBER			
	I		II	
Sample of plant powder taken, grams	1.0		0.1900	
Extract make up to volume, cc.	250		250	
Aliquot taken, cc.	12.5	25	50	75
Iodine titration in aliquot, cc.	6.0	13.3	5.4	8.4
Iodine found in aliquot, grams	0.0038	0.00844	0.00343	0.00533
Starch equivalent in aliquot, grams	0.035	0.077	0.031	0.049
Total starch found in sample, grams	0.70	0.70	0.155	0.163
Percentage of starch, dry powder basis	70	77	81.6	85.8
Percentage of starch, fresh tissue basis	10.8	12.0	12.6	13.2
Percentage of starch found by official diastase method	11.62			

The average of the results from the absorbed-iodine method is close to that found by the official method[1], but the variation with the different samples and different aliquots of the same sample is large. The average deviation of a single sample is about 8 per cent of the value obtained by the diastase method, and when the true value is, say, 11.62 per cent, an error of 8 per cent, which amounts to about 1 per cent, would be too large for accurate results.

Since the dry powder contained relatively many times as much starch as the cantaloupe seed powder, small portions only could be taken for starch extractions, and small aliquots for precipitation of starch-iodide. Hence the errors of the method were multiplied many times. Thus, the error in Experiment I is 40–80 times, and that in Experiment II 60-100 times that involved in the cantaloupe seed powder procedure.

Apparently the method is not well suited to tissue containing large amounts of starch for which material the results are only approximate. One feature of the method, however, recommends it for use in such cases, namely, the necessity of drying the tissue and making a preliminary extraction to remove the sugars is avoided, thus shortening the time required to estimate the starch in a sample. It is possible that the procedure could be modified to increase its accuracy and make it applicable to such tissues.

RESULTS WITH THE RESIDUAL-IODINE METHOD.

Starch was precipitated from six samples. of 100 cc. each from a seed extract by adding iodine. (In this case, the exact amount of iodine added is of no importance, provided it is sufficient to produce precipitation.) The starch iodide precipitate was thrown to the bottom of the bottle by centrifuging. In order to apply the principle involved in Long's residual iodine method, it was necessary to partially purify the starch-iodide and remove from it the non-starch iodine absorbing substances in the seed extract, and also to remove most of the excess calcium chloride which absorbs iodine.

For this purpose the liquid above the precipitate was removed by suction, 100 cc. of distilled water added, the bottle shaken, and strong iodine solution added until an excess of iodine was present (indicated by the brown color of the foam in the bottle). When this precipitate settled, it was centrifuged again and the liquid removed by suction. This process was repeated once more and the precipitate washed into a 100 cc. volumetric flask.

To remove the iodine present in order that a measured amount of standard iodine could be added later, small quantities of thiosulfate were added and the liquid heated. By adjustment with iodine and

[1] Determinations were made by C. G. Church.

thiosulfate, a point was reached when the solution of starch was found to have an excess of neither.

To the starch solution, 10 cc. of 10 per cent potassium iodide and 20 cc. of 0.02N iodine were added, and the volume made up to 100 cc. After standing, the precipitate settled and the entire contents of the flask were poured upon a filter paper. The precipitate was not washed but the iodine in an aliquot of the filtrate was titrated with thiosulfate. The titration values obtained were as follows: 12.5, 13.1, 13.6, 14.4, 13.8, 13.8; average 13.5.

It is impossible to calculate the starch percentages from these data, because no determinations of the values obtained by known amounts of starch under similar conditions were made. The values in Table 1 can not be used because the precipitation was produced and the precipitate handled under a widely different procedure. Time to obtain values for another set of starch standards was lacking.

At present the results of duplicates upon the same seed extracts are of most interest, and the figures here reported indicate that this modification gives promise of affording the basis for a satisfactory method. The average deviation of the titration values from the mean is 0.5 cc., which is less than 4 per cent of the mean.

It was not realized until late in the course of the work that this modification could be made, and sufficient work upon it was not done. The procedure here described could be improved and made more accurate in the following way: The final addition of iodine and precipitation of the starch should be carried out in a centrifuge bottle with a volumetric graduation. After being made up to the mark and thoroughly shaken occasionally after precipitation begins, the bottle should be centrifuged and an aliquot drawn off the top for titration, the errors of filtration thus being avoided. Known amounts of starch standards may be treated in the same way and comparisons made.

The residual-iodine method is less convenient than the absorbed-iodine method because of the extra work involved in re-precipitating and centrifuging.

RESULTS OF DETERMINATIONS BY REDUCTION METHODS.

The results of the estimation of the starch in the starch-iodide precipitate by copper-reduction methods are shown in Table 7. Lot No. M. S. represents a seed extract containing relatively large amounts of starch, while Lot L. S. contained only small amounts of starch. Four aliquots of 100 cc. each were taken from Lot M. S. and 6 aliquots of 200 cc. each from Lot L. S. The starch in each was precipitated by adding an excess of iodine and the precipitate obtained at the bottom of the bottle by centrifuging. This precipitate was purified by repre-

cipitation after the addition of water and iodine in order to remove non-starch reducing substances.

TABLE 7.

Duplicate determinations by reduction methods.

LOT NO.	TITRATION VALUES		STARCH IN SEED POWDER		LOT NO.	TITRATION VALUES		STARCH IN SEED POWDER	
	Permanganate	Thiosulfate	Permanganate Method	Scales Method		Permanganate	Thiosulfate	Permanganate Method	Scales Method
	cc.	*cc.*	*per cent*	*per cent*		*cc.*	*cc.*	*per cent*	*per cent*
M. S.	5.0	14.9	1.16	1.21	L. S.	1.2	3.3	0.14	0.13
M. S.	4.4	15.6	1.02	1.28	L. S.	1.1	4.7	0.13	0.19
M. S.	3.5	14.2	0.81	1.15	L. S.	1.2	5.7	0.14	0.23
M. S.	3.5	14.0	0.81	1.13	L. S.	1.2	5.4	0.14	0.22
					L. S.	1.5	5.7	0.17	0.23
					L. S.	1.1	4.5	0.13	0.18
Avge	4.1	14.7	0.95	1.19		1.2	4.9	0.12	0.20

Found by absorbed-iodine method 1.20 Found by absorbed-iodine method 0.28

The precipitate was collected in a 100 cc. volumetric flask and thiosulfate added to break up the starch-iodide and react with iodine. By adjustment with iodine and thiosulfate, a point was reached at which the liquid had an excess of neither. Concentrated hydrochloric acid was added to make 2 per cent by weight and hydrolysis carried out for 3 hours on a boiling water bath. The acid was neutralized with sodium hydroxide and a slight excess of sodium carbonate was added to precipitate the small amount of calcium present. The volume was adjusted at 100 cc. and filtered. Aliquots of the filtrate were taken for copper reduction.

From Table 7 it will be noted that two methods were employed: (1) The ordinary Fehling's solution was used for reduction, and the cuprous oxide formed was titrated with standard potassium permanganate; (2) Scales' method modified by using 0.02N iodine and thiosulfate for titration, 20 cc. of the sugar solution and 25 cc. of the reagent for reduction. The flame was adjusted to produce boiling in 4½ minutes, and the boiling continued for 3 minutes. This procedure was standardized with pure dextrose.

Table 7 gives the results of the duplicate determinations upon the same seed extract and the results of the absorbed-iodine method. The expectation that this method would give less variable results than the absorbed-iodine method was not supported by the data. The average deviations are from 4 to 8 per cent of the mean, which is not an improvement over the results by the absorbed-iodine method.

The estimations by the Scales method gave higher values than were obtained by the permanganate method. The reason for this is not

known, but it is apparent that the Scales method is more sensitive than the permanganate method. Thus the titration ranges between the two lots of seed extracts were from 4.9 to 14.7 cc. with the Scales method, and from 1.2 to 4.1 cc. by the other; furthermore, the end-point of the titration with the Scales method is more distinct.

The percentage of starch in seed powder, calculated from the data by reduction methods, is lower than that found by the absorbed-iodine method. This may be explained as follows: (1) Not all the starch was dissolved in calcium chloride and hence not enough dextrose was represented to account for the original starch; (2) some of the starch was lost because part of the starch-iodine was carried away from the precipitate by suction; (3) some of the dextrose was destroyed by the process of hydrolysis.

To obtain an estimate of the amount of starch which can be recovered in this way, the following experiment was conducted: 0.2411 gram of pure starch was dissolved in calcium chloride in the usual way and carried through the procedure already described. The dextrose was then estimated and from it the starch represented by that amount calculated[1]. This was 0.2161 gram, which is 89.6 per cent of the original starch taken. If the percentage values in Table 7 are corrected on the basis that the amount found is equivalent to 89.6 per cent of that originally present, the values for the permanganate method become respectively, 1.06 and 0.14 per cent and the values by the Scales method become 1.33 and 0.22 per cent.

In this connection it should be stated, however, that whether or not all the starch was dissolved in calcium chloride is not a factor in the absorbed-iodine method, inasmuch as the aliquots taken in the standard determinations represented a certain proportion of the total starch originally taken.

COMPARISONS OF THE THREE METHODS.

From the experience so far gained, it is believed that the absorbed-iodine method is the most convenient as results are obtained by it in the shortest time. The reduction method (using the Scales modification), although tedious, gave promise of being improved to give greater sensitivity, since the range from 0 to 1.0 per cent can be split up into more distinct steps by means of it than by the others. The residual-iodine method exhibits the possibility of being intermediate in both respects.

SUMMARY.

A starch method that would cover the range from 0 to about 1.0 per cent starch by steps of about 0.1 per cent was needed. The methods here described, applied to cantaloupe seed powders, fulfilled this condition in a satisfactory manner.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 80.

The principal method used consisted essentially in dissolving the starch in concentrated calcium chloride solution, precipitating the starch under a standard set of conditions, titrating the iodine taken up by the starch, and comparing the values thus obtained with those given by known amounts of starch under the same conditions.

In other methods tried in a limited way, the starch was measured not by the iodine absorbed, but by the residual iodine left after absorption, and the starch present in the starch iodide was estimated by copper reduction methods after hydrolysis with acid.

Detailed descriptions of the methods are given, together with the results obtained by their use under different conditions, and suggestions as to their improvement and applicability to other kinds of tissue. For the present it is recommended only for tissues containing small amounts of starch.

ANALYSIS OF LICORICE ROOT AND LICORICE EXTRACT.

By Percy A. Houseman (Mac Andrews & Forbes Co., Camden, N. J.).

The analytical methods proposed for licorice root and extract have the defects which frequently apply to the analysis of plants and plant products—their incompleteness often prevents a correct judgment of the quality of the material under examination.

Fairly satisfactory methods have been developed for glycyrrhizin, sugars, starch and gummy matters, etc., but little has been done toward developing quantitative determinations of the less desirable constituents of licorice root and extract, viz., the resins and bitter substances.

A licorice extract made from Oriental licorice root may easily contain twice as much glycyrrhizin as one from Spanish root, and yet the former is of less desirable taste owing to the larger amount of bitter substances which it contains.

Interest has naturally centered around the sweet principle of licorice root (glycyrrhizin), since this substance has not yet been found in commercial quantity in any other plant, and it is chiefly responsible for the characteristic taste of licorice.

In a very exhaustive article, Linz[1] has considered all the noteworthy contributions to licorice analysis since the earliest ones of Pfaff and others, which dated from about 1800. He subjected twenty-seven methods for the determination of glycyrrhizin to experimental investigation and accepted only the method which was originally published by the author of this paper.

Linz particularly condemns the method proposed by Tschirch and Erikson, and in this the writer entirely agrees with him. Linz then

[1] *Arch. Pharm.*, 1916, 254: 65, 204.

passes on to the examination of licorice root and again accepts the writer's method as the only satisfactory one for the determination of glycyrrhizin in the root. He states: "Houseman's method seems to give quantitative yields of the glycyrrhizic acid, with a high degree of purity of the latter".

The writer, therefore, feels justified in publishing this paper as a summary of his investigations on licorice root and extract, which have been reported in a series of papers[1], and in bringing them up to date with the results of later experience. This is done in the hope of inducing other workers to carry on analytical work on licorice, and especially to contribute methods for the assay of bitter principles in the root and in the extract, for the separation of starch from gummy matters, etc.

ANALYSIS OF LICORICE ROOT.

The methods for moisture, total ash, ash insoluble in hydrochloric acid (sand and dirt), crude fiber and sugars require no special comment. being carried out according to the accepted methods of the A. O. A. C.[2] Resins are determined by extraction with ether. Bitter substances are extracted by cold absolute alcohol.

GLYCYRRHIZIN.

The licorice root is ground to pass a 20 or 30 mesh sieve, dried at low temperature to moisture content of not more than 2% and the resins extracted from 3 grams of powdered and dried root with ether. This may be done in the extraction apparatus of the Joint Rubber Insulation Committee[3] or in a 100 cc. centrifuge tube by stirring three times for 15 minutes each with 75 cc. portions of ether. The two procedures give identical results and the latter avoids the necessity of drying and washing a thimble.

The root from which the resins have been extracted is dried to remove ether and is stirred in the 100 cc. centrifuge tube with 75 cc. of 75% (by volume) alcohol. The 75% alcohol remains on the root not less than three hours, preferably overnight. The tube is then centrifuged for 5 minutes at 1500 R. P. M. The clear solution is poured off into a flask, the sediment stirred up with a second portion of 75 cc. 75% alcohol, centrifuged again, the liquor poured off and a third similar treatment given with 75% alcohol. The combined three liquors are evaporated just to dryness from a steam bath and the alcohol recovered. A vacuum is preferred towards the end. The residue in the flask is dissolved in 10 cc. of hot water and the solution filtered through a small filter paper into a centrifuge tube with a mark at 20 cc. The flask and filter paper are washed and the volume made to the 20 cc. mark.

The filtrate is cooled to 15°C., and the glycyrrhizin is precipitated with 3 cc. of 10% (by weight) sulfuric acid. The tube is allowed to stand in the ice-box overnight and is then packed in cracked ice for half an hour. The tube is centrifuged for half a minute, and the clear liquid is poured off. The precipitate is stirred up with 5 cc. of ice-water saturated with ether, centrifuged again for half a minute, and the clear liquid poured off. The sediment is again stirred up with 5 cc. of iced ether-water, centrifuged, and the clear liquid poured off as completely as possible. The tube is kept

[1] *Am. J. Pharm.*, 1912, **84**: 531; 1916, **88**: 97; 1921, **93**: 481.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920.
[3] *J. Ind. Eng. Chem.*, 1914, **6**: 75.

cold throughout the operation and all the glycyrrhizin is retained in the tube. Thirty cc. of warm 95% alcohol are added to the washed glycyrrhizin in the tube. This solution is retained to be united later to the second precipitate of glycyrrhizin. To get this, the liquor and two washings, obtained as above, are combined and neutralized with ammonia, evaporated to about 5 cc., transferred to a centrifuge tube, made to 10 cc., cooled and precipitated with 2 cc. of 10% sulfuric acid. After standing in the ice-box overnight, the tube is packed in ice for half an hour, centrifuged, and the clear liquor poured off. The glycyrrhizin is stirred up with 5 cc. of iced ether-water, centrifuged half a minute, and the liquor poured off. A second washing with ice-cold ether-water is given, using 3 cc. The precipitated glycyrrhizin is dissolved in 10 cc. of warm 95% alcohol. Both portions of dissolved glycyrrhizin are then filtered through a 70 mm. No. 40 Whatman paper into a weighed glass dish. A small amount of gummy matter not soluble in 95% alcohol remains on the paper. The tubes and paper are washed with warm 95% alcohol and the washings added to the dish. Two drops of 5% ammonia are added to neutralize any traces of sulfuric acid. The solution in the dish is then evaporated to dryness and the glycyrrhizin weighed, after drying at 100°C. overnight. When a more rapid method of analysis is desired, each portion of precipitated glycyrrhizin may be allowed to stand for 3 hours instead of overnight. The difference in the result is hardly appreciable.

The glycyrrhizin weighed is fairly pure and there seems no practicable method of purifying it further, at any rate for technical-analytical purposes. The process of redissolving the glycyrrhizin in dilute ammonia and reprecipitating with sulfuric acid does not achieve a very notable increase in purity and is coupled with unavoidable losses. In the method described above, it is considered that the losses due to solubility of glycyrrhizin in ice-cold ether-water are about balanced by the impurities in the glycyrrhizin weighed.

TREATMENT OF LICORICE ROOT WITH SOLVENTS.

(1) *Petroleum Ether* extracts less than 1 per cent of a semisolid grease of bitter taste and unpleasant odor. On long standing, needle-shaped crystals, which are insoluble in ether and may be crystallized from warm benzene or chloroform, are deposited. The crystals have not been further examined.

(2) *Chloroform.* When a chloroform extract of licorice root is evaporated, a mixture of colorless crystals with a yellow fatty substance is obtained. The latter is removed with ether, and the crystals are purified by crystallizing from chloroform. The yield of pure crystals was 0.1 per cent.

(3) *Ether*, used after petroleum-ether, removes from licorice root from 1.5 to 5.0 per cent of resins; roots from Spain, Italy, Greece, Anatolia and Mesopotamia yield the lower figures and those from Russia, Syria and China the higher. No glycyrrhizin is removed by ether.

It is of interest to note that the resins are confined to the *bark* of the root.

(4) *Alcohol.* Cold 95 per cent alcohol removes no glycyrrhizin from licorice root, the glycyrrhizic acid being present as calcium and potassium salts. After the resins are removed by ether, cold 95 per cent alcohol yields about 8 to 11 per cent of extracts, consisting chiefly of bitter principles, together with a small amount of sugars. The glycyrrhizin may then be quantitatively removed by cold 75 per cent by volume alcohol, but it is found advisable in practice to omit a preliminary extraction with 95 per cent alcohol, because it does not seem to lead to a purer glycyrrhizin, and has the disadvantage of leaving the latter, when finally precipitated, in a granular form in which serious losses during the subsequent washing with ice-cold ether-water can hardly be avoided. The same objection applies to preliminary extraction with absolute alcohol (hot or cold), and to alcohol to which a small quantity of ammonia has been added. The preliminary removal of resins with ether does not have this objectionable feature and is desirable. For these reasons the quantitative procedure already outlined has been adopted.

The glycyrrhizin so prepared is of a light brown color, has an intensely sweet taste and is evidently nearly pure. The amount usually varies from 6 to 10 per cent of the root, Spanish and Italian roots giving the lower figure and Oriental roots the higher. One sample of Anatolian root examined showed no less than 13 per cent of glycyrrhizin. Most of the figures published in the literature for glycyrrhizin in licorice root are decidedly too low. The glycyrrhizin extracted by dilute alcohol, after resins and bitter principles have been removed by ether and 95 per cent alcohol, forms a very satisfactory material from which to prepare the pure, white glycyrrhizin described by Tschirch and Cederberg[1] and Tschirch and Gauchmann[2]. It may be noted that no glycyrrhizin is found in that part of the licorice plant which grows above the ground.

Saponin. A haemolytically active saponin occurs in the inner bark of the root, but not in the outer bark, nor in the central part of the root. The presence of a saponin may be shown by evaporating to dryness a 75 per cent alcohol extract of the root, treating the dry extract with cold water, and testing in the regular way with sheep- or ox-blood.

Asparagin has also been found in licorice root in small quantity, as well as a number of sugars.

Tannins. Tests with hide powder show that only a very small amount of tannin is present in licorice root.

A yellow dye is present in the root which dyes silk a pale, but fast, yellow. The root is percolated with hot water, the solution evaporated to dryness and the residue extracted with absolute alcohol. The alco-

---

[1] *Arch. Pharm.*, 1907., **245**: 97.
[2] *Ibid.*, 1908, **246**: 545; 1909, **247**: 121.

hol is evaporated and the dry extract treated with hot water. This aqueous solution dyes silk yellow.

ANALYSIS OF LICORICE EXTRACT.

This analysis comprises moisture, ash, matters insoluble in cold water and in hot water, starch and gums, glycyrrhizin and sugars.

Matters insoluble in cold water.

Two grams of the licorice mass are weighed into a small copper-gauze basket, which is suspended in a 100 cc. centrifuge tube. The tube is nearly filled with cold water, and when the paste is completely disintegrated (after about 18 hours) the basket is agitated, washed and removed. The contents of the tube are whirled in an electrical centrifuge for 10 minutes at about 1500 R.P.M. The clear liquor is poured off, and the sediment stirred up with fresh water and whirled in the centrifuge for a further 10 minutes. The liquor is again discarded, and the sediment is washed into a weighed glass dish and evaporated. The residue, dried in an oven at 100–105°C. for 24 hours, is weighed.

The proportion of water-insoluble material increases markedly with the age of a licorice paste containing 25 per cent moisture. A sample showing, say, 5 per cent when freshly made, is likely to give double that figure when a month or two old, due to deposition of insoluble starch. This increase is much smaller on a licorice mass containing less than 20 per cent moisture.

Matters insoluble in hot water.

Two grams of licorice mass are placed in a 150 cc. beaker, boiled for 5 minutes with 80 cc. of water and the solution transferred to a 100 cc. centrifuge tube. The tube and contents are centrifuged for 10 minutes at 1500 R.P.M., the liquor poured away, and the sediment washed into the beaker and boiled 5 minutes with 80 cc. of water. The centrifuging is repeated, the liquor discarded again and the sediment washed into a weighed glass dish, evaporated, dried and weighed.

STARCH, GUMS AND GLYCYRRHIZIN.

The procedure for glycyrrhizin follows closely that given for root, but since most of the resins are left in the spent root in the process of manufacture, it is not necessary to extract with ether, as is done in the determination of glycyrrhizin in licorice root.

Two grams of licorice extract in a 100 cc. centrifuge tube are allowed to stand overnight with 15 cc. of water at room temperature. The mass is then stirred until completely disintegrated; 15 cc. of 75% (by volume) alcohol and 53 cc. of 95% alcohol are added from a buret with stirring, to precipitate the starch and gums. This gives a mixture containing 75% (by volume) alcohol when the licorice extract contains 25% moisture. After standing not less than 3 hours, the tube is centrifuged for 5 minutes at a speed of about 1500 R.P.M. The clear solution is poured off into a flask, the sediment is stirred up with 75 cc. of 75% (by volume) alcohol, centrifuged again and the clear solution is poured off. The sediment is stirred up a second time with 75 cc. of 75% alcohol, centrifuged, and the solution is again poured off. The precipitated starch and gums are washed into a tared dish, dried and weighed. The combined

three liquors are then treated in the same manner as those from licorice root, except that in precipitating the first (main) fraction of glycyrrhizin, the aqueous solution is made up to 30 cc. instead of 20 cc.

A weaker alcohol than 75 per cent should not be used, as some starch and gums then escape precipitation. A stronger alcohol should also not be used, as it has been found that 80 per cent alcohol actually precipitates a little glycyrrhizin with the starch and gums in some cases.

It is more important to obtain all the glycyrrhizin even at the expense of a slightly low figure for starch and gums, than to obtain all the starch and gums at the expense of a slightly low figure for glycyrrhizin.

A comparison of the glycyrrhizin content of root with that of the commercial extract made therefrom shows clearly that considerable decomposition of glycyrrhizin occurs in the treatment of licorice root with boiling water.

P. Bertold[1] claims that the glycyrrhizin in licorice extract was reduced from 19.22 per cent to 12.03 per cent when "ordinary" water was used to extract the root instead of distilled water. This claim for the harmful effect of hard water seemed so extravagant that his results were checked, using distilled water, Camden (N. J.) city water, and artificially hardened water, the latter being saturated with calcium and magnesium carbonates and with calcium sulfate, while carbonic acid gas was bubbled in.

All the results were calculated to the basis of 25 per cent moisture in the licorice extract and were as follows:

	Per Cent Glycyrrhizin in Extract
Root extracted with distilled water	20.4
" " " Camden city water	19.8
" " " artificially hardened water	19.5

These results show that within experimental error there is practically no loss of glycyrrhizin when "ordinary" water, instead of distilled water, is used to extract licorice root.

SUGARS.

Sugars are determined in a portion of the original licorice mass, using normal lead acetate and following the official method of the A.O.A.C.[2]

SUMMARY.

Analytical methods are given for licorice root and extract, with further remarks on various constituents extracted by solvents and not determined quantitatively.

---

[1] *Giorn. chim. ind. applicata*, 1921, **3**: 490; *Chem. Abstr.*, 1922, **16**: 2573.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 73.

VARIATIONS IN THE CONCORD GRAPE DURING RIPENING.

By H. A. NOYES, H. T. KING and J. H. MARTSOLF[1] (Mellon Institute of Industrial Research, Pittsburgh, Pa.).

A leading grape juice concern makes routine determinations of sugar in the Concord grape as it ripens. These analyses, previous to 1920, were stopped as soon as factory pressing of grapes commenced. In only a few instances were samples taken from the same vineyard; therefore no predictions could be made from the incomplete data as to how grapes would ripen in an off year or what their composition would be the latter part of the pressing season.

The work reported in this paper is a part of that undertaken to find out how to manufacture a more uniform Concord grape juice. The literature on the changes in composition of the Concord grape shows that the analytical results obtained in the laboratory are more uniform than those obtained in factory practice. The figures given are practically a complete record of analyses where daily changes were made in factory operation to give the best juice. As the analyses during 1919 showed no regularity additional data were procured in the two following years under different conditions of growth and maturity. Since temperature changes in the factory process are necessary as the pressing season advances, the relative differences in the same sample of grapes when analyzed entire, pressed out cold or pressed out hot give data on the changes in composition during ripening as well as a basis for adjusting factory operations with fruit in different degrees of maturity.

The season of 1920 was wet and cool, and many growers in the Chautauqua and Erie grape belt were of the opinion that grapes would not reach a satisfactory sugar content for the manufacture of grape juice. A study of the factory records for previous years showed that grapes had not appreciably increased in sugar content after the first of October. Results of analyses of the Concord grape at different stages of ripening have been reported by W. B. Alwood[1] and the following collaborators of the United States Department of Agriculture: B. G. Hartmann, L. M. Tolman, J. R. Eoff, M. J. Ingle, S. F. Sherwood, J. O. Carrero and T. S. Harding. The figures obtained by these workers were more uniform than those obtained by analyzing daily samples of grape juice during a factory pressing season but were from scattered vineyards and covered irregular intervals of time.

To get detailed information as a basis for future work, two vineyards were selected in the town of Westfield, New York, for the taking of

---

[1] Based on a paper presented before the Division of Agricultural and Food Chemistry at the meeting held in Rochester, N. Y., April, 1921.

[1] U. S. Bur. Chem. Bulls. 140: (1911); 145: (1911). U. S. Dept. Agr. Bulls. 335: (1916); 452: (1916); 656: (1918).

special sets of grape samples from the time the grapes began to show color until the harvest was completed. Both vineyards were mature; one had received good care during the seasons of 1919 and 1920, had a high yield and was in good balance of fertility, while the other had had average care and bore a representative (average) crop for 1920.

A certain part of each vineyard was set apart for sampling, and no grapes were harvested from these sections until after all the season's samples were taken. Three times a week—Monday, Wednesday and Friday mornings—samples were obtained. A series of vines where the fruit appeared to be in an average state of ripeness for that date was chosen. From eight to ten pounds of grapes were picked and brought to the laboratory. Analyses were started immediately and the results reported are averages for both vineyards.

EXPERIMENTAL WORK.

In 1919 grapes were of uniformly high quality throughout the grape belt and a large number of factory experiments were started with the idea of improving commercial grape juice by employing new methods of processing. As checks on this work several five-gallon samples of each

TABLE 1.

Analyses of factory-run grape juice, 1919.

DATE	SUGARS	ACIDS AS TARTARIC	TANNING AND COLORING MATTER
1919	*per cent*	*per cent*	*per cent*
9-23	16.09	0.975	0.303
9-25	15.99	1.045	0.352
9-27	16.56	1.062	0.332
9-29	16.74	0.984	0.418
9-30	16.45	1.002	0.311
10-1	16.70	0.946	0.364
10-2	16.75	0.937	0.344
10-3	16.81	0.951	0.315
10-4	17.14	1.011	0.325
10-6	16.69	0.892	0.299
10-7	17.00	0.886	0.344
10-8	16.49	0.901	0.303
10-9	17.38	0.886	0.323
10-10	17.02	0.892	0.303
10-11	16.62	0.920	0.354
10-13	17.21	0.886	0.336
10-14	15.77	0.897	0.342
10-15	16.82	0.879	0.375
10-16	16.94	0.883	0.321
10-17	17.17	0.849	0.317
10-18	17.60	0.812	0.313
10-20	16.24	0.821	0.297
Average	16.73	0.923	0.331
High	17.60	1.062	0.418
Low	15.77	0.812	0.299
Variation	1.83	0.250	0.119

day's regular factory production of grape juice were set aside for observation. The results of tests made on these samples are shown in Table 1.

Table 1 shows that there is no regular systematic change in the composition of grape juice pressed at different times during a regular factory pressing season of approximately twenty days. This may be surprising to some since it might be expected that the grapes would get uniformly sweeter or uniformly less acid each day as the season progressed.

The general tendency is for sugars to increase and for acids to decrease when the grapes are left on the vines. Tannin and coloring matter are problems for future study, but it is certain that the substances affecting these determinations are not uniform throughout the season. For example, if tannin formation and liberation is proceeding one way, if a certain class of coloring matter is proceeding another way, and if these two are associated in any way with sugar and bitartrate formation, irregular results will follow.

In 1920 investigations were undertaken from three different angles, as follows: 1, That of the whole fruit; 2, the cold-press juice; 3, the hot-press juice. The determinations made on the whole fruit were average weight of the individual berry, moisture content and sugar content. Both the hot and cold juices were analyzed for total acids, tannin and coloring matter, and sugar. Records were made of Brix readings and those other regular determinations which are usually either made or calculated.

METHODS OF PROCEDURE.

Whole grapes.—The average weight per berry was determined by weighing 100 berries immediately after picking from the stems. Moisture was determined by weighing 10 average berries on an analytical balance, crushing them in a tared container and drying at 100°C. to constant weight. Sugar was determined by the reduction method[1].

Preparation of juice.—Two lots of stemmed grapes were macerated. One lot was pressed at room temperature and the juice was known as cold-press; the other lot was heated for five minutes at 145°F. before pressing. This was known as the hot-press juice. In 1920 all pressing was done by hand[2], and the results secured by previous workers[3] led to the belief that a representative juice was obtained. In 1921 a small hand press was used. After being brought to room temperature the juice samples were analyzed for sugar, total acids, and tannin and coloring matter, using the regular official methods[4].

Table 2 shows that—

(1) There was no great variation in the weight of the berry as ripening advanced.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 155.
[2] U. S. Bur. Chem. Bull. **145**: (1911).
[3] Univ. Calif. Pub., 1918, **3**: 103.
[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 153.

TABLE 2.

Analyses of grapes and cold- and hot-press juice on different dates, 1920.

DATE	GRAPES			COLD-PRESS JUICE			HOT-PRESS JUICE		
	Weight of Berry	Moisture	Sugar	Sugar	Acid	Tannin and Coloring Matter	Sugar	Acid	Tannin and Coloring Matter
1920	*grams*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
9–13....	3.22	85.82	7.89	9.22	1.89	0.043			
9–15....	3.02	84.32	7.72	9.52	1.66	0.027			
9–17....	2.95	84.03	9.10	10.51	1.43	0.066			
9–20....	2.74	83.86	10.61	11.99	1.30	0.041	12.09	1.53	0.208
9–22....	3.13	84.70	9.57	11.77	1.40	0.039	11.70	1.81	0.164
9–24....	3.05	82.04	13.34	13.44	1.35	0.063	13.12	1.61	0.176
9–27....	3.23	82.42	12.90	13.20	1.37	0.062	13.25	1.55	0.144
9–29....	3.01	83.05	11.10	12.99	1.18	0.038	13.14	1.44	0.158
10–1.....	3.00	84.44	10.69	12.94	1.00	0.039	12.97	1.29	0.141
10–4.....	3.34	83.37	10.97	13.44	1.09	0.053	13.49	1.33	0.149
10–6.....	3.16	82.03	13.25	13.40	1.10	0.033	15.21	1.37	0.116
10–8.....	3.08	81.70	12.59	14.02	0.95	0.044	14.25	1.31	0.169
10–11....	3.03	82.53	12.81	13.15	1.03	0.047	13.94	1.30	0.150
10–13....	3.40	81.51	12.94	14.82	1.02	0.061	14.47	1.22	0.141
10–16....	3.07	81.53	13.40	15.06	0.98	0.064	15.09	1.21	0.207
10–18....	3.13	81.30	12.82	16.00	0.92	0.043	16.52	1.17	0.190
10–20....	2.81	82.24	12.41	15.62	0.88	0.062	16.48	1.00	0.103

(2) The moisture content of the grapes decreased somewhat as the season advanced but was not directly proportional to the increase in the sugar content.

(3) The sugar content of the grapes increased, in general, as the ripening period advanced. After ripening had reached a certain point the changes in sugar content were irregular.

(4) The juices pressed out from grapes by both the cold and hot processes showed increases in sugar and decreases in acid as ripening continued.

(5) Tannin and coloring matter were irregular in both the cold- and hot-press juice but ran much higher in the hot-press.

The effects of season are readily apparent as we compare Tables 2 and 3. The ripening commenced almost a month earlier in 1921 than it did in 1920.

The following outstanding points are brought out in Table 3:

(1) As in 1920 no large variation in the weight of berry was found but a tendency towards increase in weight as the season advanced was noted. The individual grape berry for 1921 was lighter than in 1920.

(2) Moisture content of the grapes decreased as ripening progressed but, as in 1920, increases in sugar content were larger than the moisture decrease.

(3) Cold- and hot-press juices gave increased sugar content and decreased acid content as ripening proceeded. This is similar to the results of 1920 but the changes in acid in 1921 were greater.

(4) Tannin and coloring matter determinations were irregular. The differences in the tannin and coloring matter content of the cold-press juice for the two years do not appear significant. The tannin and coloring matter of the hot-press juice of 1921 was higher than that of 1920.

TABLE 3.

Analyses of grapes and cold- and hot-press juice on different dates, 1921.

DATE	GRAPES			COLD-PRESS JUICE			HOT-PRESS JUICE		
	Weight of Berry	Moisture	Sugar	Sugar	Acid	Tannin and Coloring Matter	Sugar	Acid	Tannin and Coloring Matter
1921	*grams*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
8–17.....	2.33	86.69	5.59	6.77	2.58	0.055	6.81	2.87	0.142
8–19.....	2.44	86.45	5.80	7.94	2.23	0.062	7.91	2.50	0.164
8–22.....	2.38	85.89	5.58	9.16	2.00	0.073	9.34	2.24	0.254
8–24.....	2.35	85.81	6.25	9.45	1.88	0.081	9.09	2.36	0.263
8–26.....	2.34	83.22	8.03	lost	1.66	0.049	lost	1.94	0.251
8–29.....	2.47	82.43	9.81	12.34	1.33	0.103	11.94	1.77	0.303
8–31.....	2.42	81.12	8.39	12.68	1.21	0.042	12.24	1.69	0.214
9–2.....	2.71	82.22	8.12	13.96	0.95	0.045	13.23	1.43	0.207
9–5.....	2.62	83.46	6.04	15.00	0.91	0.045	14.14	1.32	0.259
9–7.....	2.80	83.80	10.58	13.96	0.77	0.031	13.16	1.23	0.279
9–9.....	2.66	82.15	12.19	16.25	0.68	0.039	15.50	1.18	0.267
9–12.....	2.80	81.20	12.21	16.38	0.75	0.054	16.87	1.19	0.370
9–14.....	2.81	81.08	13.26	16.10	0.71	0.044	15.64	1.15	0.236
9–16.....	2.87	82.40	12.36	16.82	0.62	0.032	14.78	1.02	0.250

DISCUSSION.

The object of the work reported in this paper was to get some fundamental information that might be applied to the commercial manufacture of grape juice. It is well known that the manufacturer of a synthetic beverage can make a more uniform product than the pure fruit manufacturer. The great differences in size of crop, quality of fruit and character of fruit juice that may be directly attributed to seasonal conditions are worthy of study. As it was thought that certain cultural practices and fertilizer treatments might possibly overcome the seasonal variations in part, an effort was made to ascertain what the differences are under supposedly good vineyard conditions. The work will be continued and the results compared with those obtained with grapes that have been grown under special vineyard conditions.

The laboratory records of the largest grape juice manufacturer in America show that the average number of harvesting days for a year's grape crop is between twenty and twenty-five. From 1904 to 1920, the recorded dates on which grapes were first considered ready for com-

mercial pressing of juice show that the earliest date was September 22 and the latest October 15. Records obtained by investigators of the United States Department of Agriculture and from the company's control laboratory show that grapes from different sections of the country vary in the proportions of acid to sugar present as well as in the total amounts of these two constituents so important in commercial grape juice.

The authors' observations are that the weight of the individual berry is not of great significance. In a good season certain vineyards will be found with smaller berries that are equally as sweet as the larger grapes. The generalization seems to be that the vineyard with a "high productivity balance" yields berries of larger unit weight.

Gore[1] reports the presence of small amounts of sucrose in the Concord grape. These determinations were made by the polarization method and no sucrose was obtained in the same samples by the reduction method. Work by the authors of this article and the results reported by Alwood[2] failed to show the presence of sucrose in the Concord grape. The work of Martinand[3] shows that an inverting enzyme, sucrase, occurs in all parts of the vine, fruit, leaves, stalks and roots. He concludes that this enzyme occurs in grape must in sufficient quantity to invert sucrose. The authors do not know the exact temperature at which this enzyme is killed but take the work of Martinand to show that fresh grape juice should not contain any sucrose. Hartmann and Tolman[4] make the following statement: "A pure Concord grape juice has not been found to contain sucrose".

A number of United States Department of Agriculture investigators say that "with certain reservations, sugar should increase and acid diminish as long as the leaves function properly. This, however, is not always the case, for as soon as the pedicels—the small stems which carry the berries—begin to wither, the fruit is gradually cut off from further influence of the growth processes taking place in the plant, and its sugar content may remain fairly constant for some time. It may appear to increase by reason of evaporation of water from the berries, or in certain cases may seem to be reduced by changes induced by the respiratory processes of the fruit"[5]. It was observed by the authors during 1920-21 that the sugar content increased as the ripening period advanced but when considered from date to date the changes in sugar composition were not regular. Observations on the weather during the period of ripening led to the conclusión that cold cloudy days retarded sugar formation, while warm sunny days accompanied by cool nights

[1] *J. Ind. Eng. Chem.*, 1909, **7**: 436.
[2] U. S. Bur. Chem. Bull., **145**: (1911).
[3] *Compt. rend.*, 1907, **144**: 1376.
[4] U. S. Dept. Agr. Bull., **656**: (1918).
[5] U. S. Bur Chem. Bull. **140**: (1911); U. S. Dept. Agr. Bull. **335**: (1916).

seemed to be most favorable to the development of sugar. The conclusion of the Department of Agriculture workers quoted is confirmatory evidence both of the results obtained in this work and of the statement that sugar formation is associated with weather conditions that have an influence on the photosynthesis of the plant.

The work of Alwood and his collaborators, of Brunet[1] and that reported in this paper all agree that sugars increase as ripening progresses and that acids decrease during the same period. From a study of the work of different investigators it may be concluded that the decrease in acid is inversely proportional to the increase in sugar. This is corroborated by the data reported in Tables 2 and 3 and shown in Graphs 1 and 2, although less intervals of time were covered between samplings than other investigators used. Processes which have not been investigated may accompany the changes in acid and sugar content of ripening grapes.

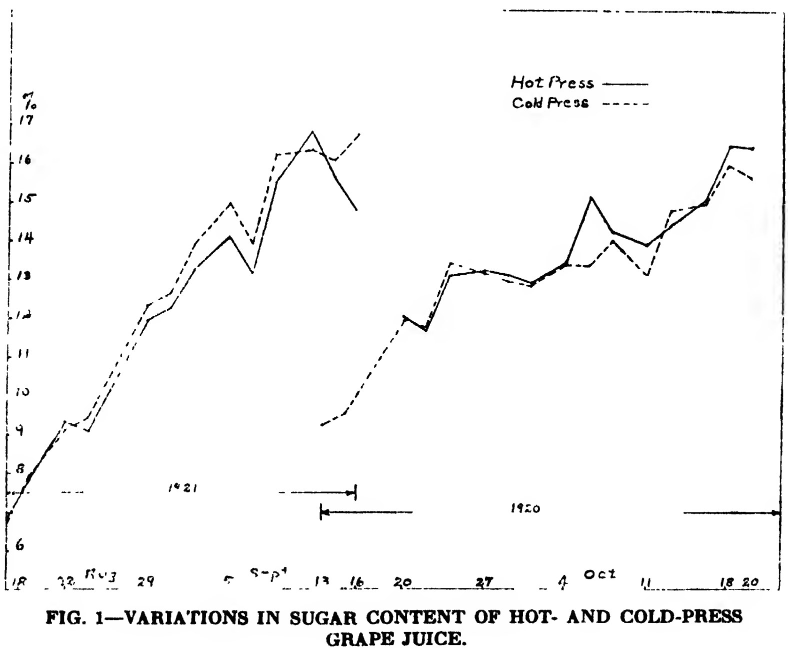


FIG. 1—VARIATIONS IN SUGAR CONTENT OF HOT- AND COLD-PRESS GRAPE JUICE.

No attempt will be made to explain the ups and downs in tannin and coloring matter determinations, Graph 3. Rosenstiehl[2] reports that the coloring matter of unfermented must is soluble but that air renders it insoluble. The extent to which air penetrates the ripe grape and renders coloring matter insoluble has not been studied by the authors of

[1] *Rev. Vit.*, 1912, **37**: 15.
[2] *Boll. chim.-farm.*, 1914, **53**: 740; *Chem. Abstr.*, 1916, **10**: 2023.

this paper. Hot-press juice in 1921 gave a much higher tannin and coloring matter determination than cold-press juice, which might be interpreted as showing that heat has something to do with making

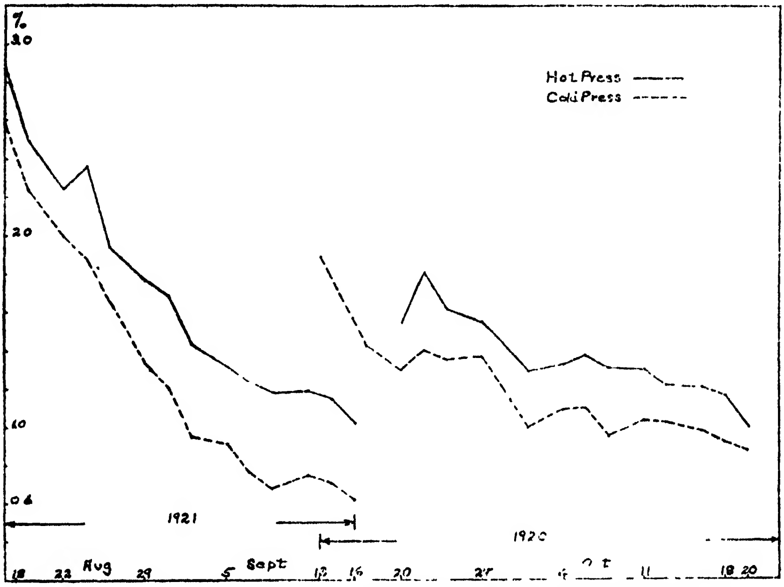


FIG. 2—VARIATIONS IN ACID CONTENT OF HOT- AND COLD-PRESS GRAPE JUICE.

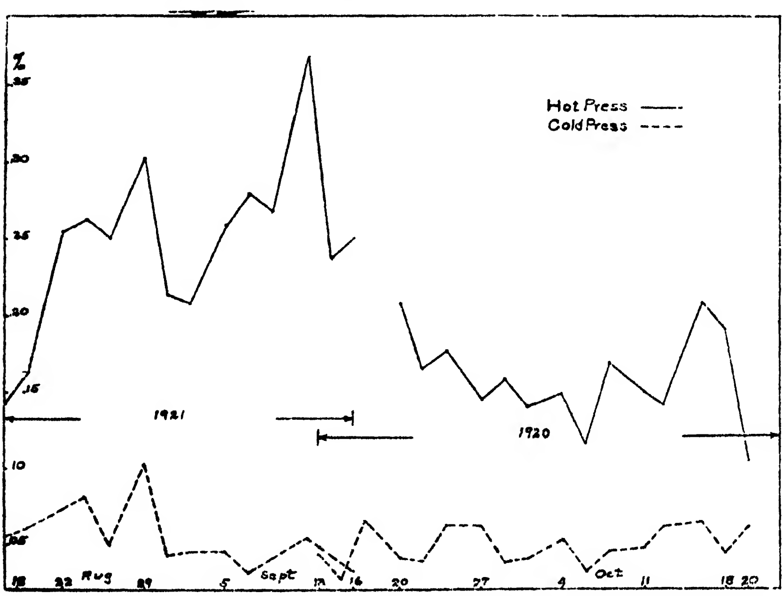


FIG. 3—VARIATIONS IN TANNIN AND COLORING MATTER OF HOT- AND COLD-PRESS GRAPE JUICE.

coloring matter soluble even after it has been thrown out of solution by the action of air.

SUMMARY.

(1) Ripening Concord grapes vary greatly in composition. This variation can not be correlated with season and date of harvesting.

(2) The weight of the individual berry remains fairly constant during ripening although it tends to increase slightly.

(3) The sugar content of the Concord grape and grape juice increases as ripening advances.

(4) The acid content of Concord grape juice decreases as ripening advances.

(5) Changes in the acid and sugar content of the Concord grape and grape juice are not regular from harvesting date to harvesting date.

(6) The tannin and coloring matter content of Concord grape juice is very irregular.

(7) Hot pressing increases the tannin and coloring matter content of Concord grape juice.

THE DETERMINATION OF CRUDE FIBER IN PREPARED MUSTARD[1].

By C. A. CLEMENS (South Dakota Food and Drug Department Laboratories, Vermilion, S. D.).

In food regulatory work the advantage of any doubt is always given to the manufacturer of an article. Consequently, while examining several samples of prepared mustard, it seemed advisable to take into consideration the statement made by M. C. Albrech[2] in regard to crude fiber determination, that "samples of prepared mustard which contained little oil gave better results than samples which contained a larger amount, showing clearly that the oil interferes with the method, and gives results much too high"; and further that, "it has been shown that the official method for the determination of crude fiber in prepared mustard is fundamentally defective, giving high results because the oil is not extracted before treatment with acid, as in the usual method". The evidence submitted in support of these statements is meager and apparently all the examples given are on samples of the same, or nearly the same, composition. In view of this fact, the official method could not be discarded without further investigation and therefore the work presented in this paper was undertaken.

[1] This report is an abstract of a thesis presented in partial fulfilment of the requirments for the degree of Master of Arts, University of South Dakota.
[2] *J. Ind. Eng. Chem.*, 1920; 12: 1175.

A summary of the analytical data on the thirty-two commercial samples of prepared mustard which were used in this investigation is given in Table 1. The methods used were those of the Association of Official Agricultural Chemists[1].

TABLE 1.

Analytical data on 32 samples of prepared mustard.

ON SAMPLES AS RECEIVED	Maximum	Minimum	Average
	per cent	*per cent*	*per cent*
Solids	25.95	11.63	17.02
Ash	5.40	2.54	3.72
Salt	4.35	1.40	2.90
Acidity	4.51	2.36	3.19
Ether extract	7.25	1.35	4.27
Protein	5.83	1.25	3.50
Carbohydrates	3.51	1.74	2.25
Crude fiber	1.75	0.60	1.23
Moisture-salt-fat-free-basis.			
Ash	8.1	4.4	6.1
Protein	44.9	18.3	33.5
Carbohydrates	35.7	16.6	22.7
Crude fiber	21.2	5.0	12.6
Moisture-salt-free-basis.			
Ether extract	37.5	14.0	28.1
Moisture-fat-free-basis.			
Ash	42.7	11.6	28.4

Difficulties were immediately encountered when the Albrech method was tried. When treated with hot water the mustard formed a colloidal-like solution which was slow in filtering, and when filtered, packed on the filter paper in such a manner that it could seldom be removed without considerable loss of mustard or the removal of a portion of the filter paper along with the mustard.

The object of the treatment suggested by Albrech is the removal of the oil from the prepared mustard before the determination of crude fiber. His procedure can be modified in such a manner as to avoid the difficulties just mentioned and at the same time accomplish the removal of the oil from the mustard. The procedure found most satisfactory is as follows:

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 261.

Weigh out 10 grams of prepared mustard into a small beaker and macerate thoroughly with 95% alcohol. Wash the mustard by means of a stream of 95% alcohol onto a 12.5 cm. filter paper of firm texture but not hardened, to which suction is applied, the tip of the filter paper being protected by a platinum cone. Wash the mustard two or three times with ether and transfer the filter paper containing the mustard to a Johnson or similar fat extractor and extract with ether for not less than 1 hour. Remove and transfer the main bulk of the mustard to the digestion beaker, break up somewhat and drive off the ether by gentle heating. A steam radiator was found convenient for this purpose. The papers containing the remainder of the mustard are also allowed to dry, after which the mustard is easily washed off into the beaker by means of a stream of 1.25% sulfuric acid. The mustard is now treated as in the official method.

This method was tried out on thirty-two different samples of prepared mustard. In nearly every case a lower result than that given by the A. O. A. C. method was obtained. However, there was no correlation between the fat content of the samples and the differences between the crude fiber determinations by the two methods. This is readily shown by Table 2.

TABLE 2.

Comparison of the results by the A. O. A. C. method and the proposed method.

NUMBER	CRUDE FIBER		DIFFERENCE	FAT	SALT	SOLIDS
	A. O. A. C. Method	Proposed Method				
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
21-143	1.62	1.38	−0.24	3.82	1.82	14.69
21-144	1.03	0.91	−0.12	7.23	2.83	23.05
21-145	1.67	0.93	−0.74	4.18	2.94	16.34
21-148	1.46	1.54	+0.08	3.50	3.37	17.25
21-149	1.03	0.92	−0.11	6.05	2.35	18.75
21-159	1.16	1.12	−0.04	5.61	2.27	19.35
21-167	1.75	1.12	−0.63	2.41	3.56	14.90
21-168	1.58	1.25	−0.33	1.37	2.38	12.17
21-169	1.48	1.15	−0.33	6.56	1.40	21.88
21-170	1.27	1.05	−0.22	3.90	2.90	18.09
21-172	1.50	1.42	−0.08	4.16	4.35	20.24
21-173	1.38	1.23	−0.15	4.43	3.15	17.23
21-174	1.44	1.26	−0.18	1.35	4.00	12.14
21-175	1.51	0.95	−0.56	4.12	3.47	17.31
21-181	1.06	0.91	−0.15	3.78	3.34	16.45
21-183	1.57	1.14	−0.43	7.25	1.76	21.38
21-185	1.29	0.79	−0.50	4.47	3.20	17.59
21-186	1.63	1.08	−0.55	3.38	2.96	14.76
21-224	1.10	0.86	−0.24	6.78	4.08	22.16
21-225	0.98	1.00	+0.02	1.37	3.42	11.26
21-230	1.58	1.00	−0.58	4.91	2.49	17.42
21-231	1.06	0.94	−0.12	1.67	3.39	11.63
21-232	1.27	1.02	−0.25	3.12	2.73	14.63
21-235	1.48	1.21	−0.27	7.04	4.20	25.95
21-239	1.19	0.74	−0.45	3.03	3.07	14.72
21-246	0.97	0.69	−0.28	3.04	2.91	14.29
21-249	0.60	0.85	+0.25	7.04	2.98	21.92
21-250	0.87	0.82	−0.05	5.93	2.51	20.10
21-251	0.90	0.84	−0.06	6.22	3.47	20.61
21-252	0.88	0.65	−0.23	5.64	2.88	19.74
21-253	1.16	1.18	+0.02	3.36	2.71	16.48

Inasmuch as materials other than fat are removed by both the Albrech method and the method proposed in this paper, it is not obvious that fat is the interfering agent but rather, it would seem, that several other factors enter in, such as acetic acid, salt and water.

Known amounts of mustard oil were added to several samples and the effect on the crude fiber determined. The results showed that the crude fiber generally increased with the increase in fat content in any one sample, but that the rate of increase was different in different samples.

SUMMARY.

A preliminary treatment for prepared mustard to be used in the crude fiber determination has been proposed.

A comparison has been made of the results obtained when the A. O. A. C. method for crude fiber has been used with and without the proposed preliminary treatment.

It has been shown that there is no correlation between the fat content of the samples and the differences between the crude fiber determinations obtained by the two procedures, and it is probable that fat is not the sole interfering agent in the A. O. A. C. method as applied to untreated prepared mustard.

PROCEEDINGS OF THE THIRTY-EIGHTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1922.

The thirty-eighth annual convention of the Association of Official Agricultural Chemists was held at the Raleigh Hotel, Washington, D. C., November 15–17, 1922.

The meeting was called to order by the President, F. P. Veitch of Washington, D. C., on the morning of November 15, 1922, at 10 o'clock.

OFFICERS, COMMITTEES, REFEREES, AND ASSOCIATE REFEREES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, FOR THE YEAR ENDING NOVEMBER, 1923.

Honorary President.

H. W. Wiley, Woodward Building, Washington, D. C.

President.

A. J. Patten, Agricultural Experiment Station, E. Lansing, Mich.

Vice-President.

R. E. Doolittle, Transportation Building, Chicago, Ill.

Secretary-Treasurer.

W. W. Skinner, Bureau of Chemistry, Washington, D. C.

Additional Members of the Executive Committee.

E. M. Bailey, New Haven, Conn.
P. B. Dunbar, Washington, D. C.

PERMANENT COMMITTEES.

Committee to Cooperate with Other Committees on Food Definitions.

JULIUS HORTVET (State Dairy and Food Commission, St. Paul, Minn.), *Chairman.*
C. D. HOWARD, Concord, N. H.
E. M. BAILEY, New Haven, Conn.

Committee to Cooperate in Revision of the U. S. Pharmacopœia.

L. F. KEBLER (Bureau of Chemistry, Washington, D. C.), *Chairman.*

H. C. Lythgoe, Boston, Mass.
H. C. Fuller, Washington, D. C.
A. R. Bliss, Emory University, Ga.
W. S. Hubbard, New York, N. Y.

Recommendations of Referees.

(Figures in parenthesis refer to year in which appointment expires.)

R. E. DOOLITTLE (Transportation Building, Chicago, Ill.), *Chairman.*

SUBCOMMITTEE A: W. H. MacIntire (1924), (University of Tennessee, Knoxville, Tenn.), *Chairman;* B. B. Ross (1926); J. W. Kellogg (1928). [Water, tanning materials and leather, insecticides and fungicides, soils (sulfur in soils), determination of active acidity in agricultural products, foods and feeding stuffs (crude fiber, stock feed adulteration, determination of starch in linseed meal and other products), saccharine products (honey, maple products, maltose products, sugarhouse products), fertilizers (borax in fertilizers, preparation of ammonium citrate, nitrogen, potash), inorganic plant constituents (sulfur and phosphorus in seeds of plants, calcium, magnesium, iron and aluminium in ash of plants).]

SUBCOMMITTEE B: E. M. Bailey (1924), (Agricultural Experiment Station, New Haven, Conn.), *Chairman;* H. C. Lythgoe (1926); A. G. Murray (1928). [Spices, limit of accuracy in the determination of alcohol, testing of chemical reagents, drugs (examination of arsphenamine and neoarsphenamine, turpentine, crude drugs, alkaloids, methods for the separation of cinchona alkaloids, laxative and bitter tonic drugs, the analysis of acetylsalicylic acid, methods for the examination of phenolphthalein, methods for the examination of procaine, methods for the examination of methylene blue, methods for the examination of pyramidon, atophan, chloramine products, determination of camphor in pills and tablets by the alcohol distillation method, determination of alcohol in drug preparations, determination of chloroform in drug preparations, analytical methods for the determination of silver in silver proteinates, determination of mercurous chloride, mercuric chloride and mercuric iodide in tablets, methods for the determination of monobromated camphor, methods for the examination of barnitaln (Veronal), methods for the determination of moisture in crude drugs, methods for the examination of benzyl benzoate, and methods for the examination of chaulmoogra oil).]

SUBCOMMITTEE C: W. C. Geagley (1924), (State Food and Drug Department, Lansing, Mich.), *Chairman;* R. E. Doolittle (1926); C. F. Whitney (1928). [Dairy products (moisture in cheese, methods for fat in malted, dried, and condensed milk), fats and oils, baking powder (fluorides in baking powder), eggs and egg products, food preservatives (saccharin), coloring matters, metals in food (arsenic), pectin in fruits and fruit products, moisture in dried fruits, canned foods, vinegars, flavors and non-alcoholic beverages, meat and meat products (separation of meat proteins, chemical examination of meat after decomposition), gelatin, cereal foods, microscopical examination of cacao products, chemical examination of cacao products, methods for the examination of cacao butter, and tea.]

Board of Editors.

R. W. Balcom (Box 290, Pennsylvania Avenue Station, Washington, D C .), *Chairman* (1926).

R. E. Doolittle (1923) R. B. Deemer (1925).
W. W. Randall (1924). W. F. Hand (1927).
Marian E. Lapp, *Associate Editor.*

Committee on Editing Methods of Analysis.

R. E. Doolittle (Transportation Building, Chicago, Ill.), *Chairman.*

B. B. Ross. J. W. Sale.
A. J. Patten. G. W. Hoover.
W. H. MacIntire.

Special Committees.

Committee on Definitions of Terms and Interpretation of Results on Fertilizers.

H. D. Haskins (Agricultural Experiment Station, Amherst, Mass.), *Chairman.*

J. W. Kellogg. G. S. Fraps.
E. G. Proulx. R. N. Brackett.

Committee to Cooperate with the American Society for Testing Materials on the Subject of Agricultural Lime.

W. H. MacIntire (Agricultural Experiment Station, Knoxville, Tenn.), *Chairman.*

J. B. Weems. F. P. Veitch.

Committee on Revision of Methods of Soil Analysis.

C. B. Lipman (Agricultural Experiment Station, Berkeley, Calif.), *Chairman.*

W. H. MacIntire. R. Stewart.
A. W. Blair. J. A. Bizzell.

Committee on Quartz-Plate Standardization and Normal Weight.

Frederick Bates (Bureau of Standards, Washington, D. C.), *Chairman.*

C. A. Browne. F. W. Zerban.

Representatives on the Board of Governors of the Crop Protection Institute of the National Research Council.

B. L. Hartwell, Kingston, R. I.
H. J. Patterson, College Park, Md.

Referees and Associate Referees.

Water:

Referee: J. W. Sale, Bureau of Chemistry, Washington, D. C.

Tanning materials and leather:

Referee: F. P. Veitch, Bureau of Chemistry, Washington, D. C.

Insecticides and fungicides:

Referee: J. J. T. Graham, Bureau of Chemistry, Washington, D. C.

Soils:

Referee: W. H. MacIntire, Agricultural Experiment Station, Knoxville, Tenn.

Sulfur in soils:

Associate Referee: W. H. MacIntire, Agricultural Experiment Station, Knoxville, Tenn.

Determination of active acidity or hydrogen ion concentration for agricultural products:

Referee: E. T. Wherry, Bureau of Chemistry, Washington, D. C.

Foods and feeding stuffs:

Referee: L. E. Bopst, Bureau of Chemistry, Washington, D. C.

Crude fiber:

Associate referee: H. H. Hanson, State Board of Health, Dover, Del.

Starch:

Associate referee: M. R. Coe, Bureau of Chemistry, Washington, D. C.

Stock feed adulteration:

Associate referee: H. E. Gensler, Department of Agriculture, Harrisburg, Pa.

Saccharine products:

Referee: H. S. Paine, Bureau of Chemistry, Washington, D. C.

Honey:

Associate Referee: S. F. Sherwood, Bureau of Plant Industry, Washington, D. C.

Maple products:

Associate referee: To be appointed.

Maltose products:

Associate referee: H. C. Gore, Bureau of Chemistry, Washington, D. C.

Sugar-house products:

Associate referee: J. F. Brewster, Sugar Station, New Orleans, La.

Fertilizers:

Referee: R. N. Brackett, Clemson Agricultural College, Clemson College, S. C.

Borax in fertilizers:

Associate referee: J. M. Bartlett, Agricultural Experiment Station, Orono, Me.

Preparation of ammonium citrate:

Associate referee: C. S. Robinson, Agricultural Experiment Station, E. Lansing, Mich.

Nitrogen:

Associate referee: I. K. Phelps, Bureau of Chemistry, Washington, D. C.

Potash:

Associate referee: A. P. Kerr, Agricultural Experiment Station, Baton Rouge, La.

Inorganic plant constituents:

Referee: A. J. Patten, Agricultural Experiment Station, E. Lansing, Mich.

Sulfur and phosphorus in the seeds of plants:

Associate referee: W. L. Latshaw, Agricultural Experiment Station, Manhattan, Kans.

Calcium, magnesium, iron, and aluminium in the ash of seed:

Associate referee: A. J. Patten, Agricultural Experiment Station, E. Lansing, Mich.

Dairy products:

Referee: J. Hortvet, State Dairy and Food Commission, St. Paul, Minn.

Moisture in cheese:

Associate referee: L. C. Mitchell, 310 Federal Office Building, Minneapolis, Minn

Methods for fat in malted milk, dried milk, and condensed milk:

Associate referee: J. T. Keister, Bureau of Chemistry, Washington, D. C.

Fats and oils:

Referee: G. S. Jamieson, Bureau of Chemistry, Washington, D. C.

Baking powder:

Referee: L. H. Bailey, Bureau of Chemistry, Washington, D. C.

Fluorides in baking powder:

Associate referee: J. K. Morton, Bureau of Chemistry, Washington, D. C.

Testing chemical reagents:

Referee: G. C. Spencer, Bureau of Chemistry, Washington, D. C.

Eggs and egg products:

Referee: R. Hertwig, Food and Drug Inspection Station, San Francisco, Calif.

Food preservatives (saccharin):

Referee: M. G. Wolf, U. S. Food and Drug Inspection Station, New York, N. Y

Coloring matters:

Referee: A. L. Burns, Bureau of Chemistry, St. Louis, Mo.

Metals in foods:

Referee: W. F. Clarke, Bureau of Chemistry, Washington, D. C.

Arsenic:

Associate referee: R. M. Hann, Bureau of Chemistry, Washington, D. C.

Pectin in fruits and fruit products:

Referee: H. J. Wichmann, U. S. Food and Drug Inspection Station, Denver, Colo.

Moisture in dried fruit:

Referee: R. W. Hilts, U. S. Food and Drug Inspection Station, San Francisco, Calif.

Canned foods:

Referee: F. C. Blanck, Bureau of Chemistry, Washington, D. C.

Cereal foods:

Referee: C. E. Mangels, Agricultural Experiment Station, Agricultural College, N. D.

Limit of accuracy in the determination of small amounts of alcohol:

Referee: H. C. Lythgoe, State Department of Public Health, Boston, Mass.

Vinegars:

Referee: H. A. Lepper, Bureau of Chemistry, Washington, D. C.

Flavors and non-alcoholic beverages:

Referee: W. W. Skinner, Bureau of Chemistry, Washington, D. C.

Meat and meat products:

Referee: C. R. Moulton, Institute of American Meat Packers, Chicago, Ill.

Separation of meat proteins:

Associate referee: C. R. Moulton,

Decomposition of meat products:

Associate referee: K. C. Falk.

Gelatin:

Referee: E. H. Berry, 5456 Ferdinand St., Chicago, Ill.

Spices:

Referee: A. E. Paul, 411 Post Office Building, Cincinnati, O.

Chemical examination of cacao products:

Referee: E. R. Miller, Room 1012 U. S. Appraiser's Stores, New York, N. Y.

Microscopical examination of cacao products:

Referee: V. A. Pease, Bureau of Chemistry, Washington, D. C.

Methods for the examination of cacao butter:

Referee: W. F. Baughman, Bureau of Chemistry, Washington, D. C.

Tea:

Referee: R. E. Andrew, Agricultural Experiment Station, New Haven, Conn.

Drugs:

Referee: G. W. Hoover, Transportation Building, Chicago, Ill.

Examination of arsphenamine and neoarsphenamine:

Associate referee: C. K. Glycart, Transportation Building, Chicago, Ill.

Turpentine:

Associate referee: V. E. Grotlisch, Bureau of Chemistry, Washington, D. C.

Crude drugs:

Associate referee: A. Viehoever, Bureau of Chemistry, Washington, D. C.

Alkaloids:

Associate referee: A. R. Bliss, Emory University, Emory University, Ga.

Methods for the separation of cinchona alkaloids:

Associate referee: E. O. Eaton, Food andDrug Inspection, San Francisco, Calif.

Laxative and bitter tonic drugs:

Associate referee: H. C. Fuller, Research Institute, Washington, D. C.

The analysis of acetylsalicylic acid:

Associate referee: A. E. Paul, 411 Post Office Building, Cincinnati, Ohio.

Methods for the examination of phenolphthalein:

Associate referee: Samuel Palkin, Bureau of Chemistry, Washington, D. C.

Methods for the examination of procaine:

Associate referee: A. W. Hanson, Transportation Building, Chicago, Ill.

Methods for the examination of methylene blue:

Associate referee: H. O. Moraw, Food and Drug Inspection Station, Chicago, Ill.

Methods for the examination of pyramidon:

Associate referee: A. W. Hanson, Transportation Building, Chicago, Ill.

Atophan:

Associate referee: W. Rabak, 311 Federal Office Building, Minneapolis, Minn.

Chloramine products:

Associate referee: W. H. Heath, Federal Building, Buffalo, N. Y.

Determination of camphor in pills and tablets by the alcohol distillation method:

Associate referee: G. H. Arner, Food and Drug Inspection Station, New York, N. Y.

Determination of chloroform in drug products:

Associate referee: C. K. Glycart, Transportation Building, Chicago, Ill.

Methods for the examination of mercurial tablets:

Associate referee: G. C. Spencer, Bureau of Chemistry, Washington, D. C.

Other associate referees for special work in drugs will be appointed by the referee.

LIST OF MEMBERS AND VISITORS PRESENT, 1922 MEETING.

Abbott, J. S., Munsey Building, Washington, D. C.
Aldrich, Elizabeth, Bureau of Chemistry, Washington, D. C.
Allen, Charles D., H. Kohnstamm Co., New York, N. Y.
Allen, R. M., Research Products Department, New York, N. Y.
Almy, L. H., Bureau of Chemistry, Washington, D. C.
Ambler, J. A., Bureau of Chemistry, Washington, D. C.
Anderson, M. S., Bureau of Soils, Washington, D. C.
Appleman, C. O., University of Maryland, College Park, Md.
Arner, G. H., Philadelphia, Pa.
Atwater, C. G., The Barrett Co., New York, N. Y.

Badger, C. H., Bureau of Chemistry, Washington, D. C.
Bailey, C. H., University Farm, St. Paul, Minn.
Bailey, E. M., Connecticut Experiment Station, New Haven, Conn.
Bailey, H. S., Southern Cotton Oil Co., Savannah, Ga.
Bailey, L. H., Bureau of Chemistry, Washington, D. C.
Bainbridge, W. C., H. Kohnstamm Co., New York, N. Y.
Balcom, R. W., Bureau of Chemistry, Washington, D. C.
Baldwin, H. B., Department of Health, Newark, N. J.
Barnes, Jesse W., Bureau of Chemistry, Washington, D. C.
Bartlett, J. M., Agricultural Experiment Station, Orono, Me.
Bates, Carleton, U. S. Gelatine Co., Milwaukee, Wis.
Bates, Frederick, Bureau of Standards, Washington, D. C.
Baughman, W. F., Bureau of Chemistry, Washington, D. C.
Beal, W. H., States Relations Service, Washington, D. C.
Benedict, L. C., Bureau of Chemistry, Washington, D. C.
Beyer, G. F., Bureau of Internal Revenue, Washington, D. C.
Bidwell, G. L., Bureau of Chemistry, Washington, D. C.
Bigelow, W. D., National Canners Association, Washington, D. C.
Birckner, V., Bureau of Chemistry, Washington, D. C.
Blaisdell, A. C., Bureau of Internal Revenue, Washington, D. C.
Boone, Paul, Department of Agriculture, Jacksonville, Fla.
Bopst, L. E., Bureau of Chemistry, Washington, D. C.
Bost, W. D., Orange Crush Company, Chicago, Ill.
Bower, J. H., 1320 Delafield St., N. W., Washington, D. C.
Boyle, Martin, Bureau of Chemistry, Washington, D. C.
Brackett, R. N., Clemson Agricultural College, Clemson College, S. C.
Bradbury, C. M., State Department of Agriculture and Immigration, Richmond, Va.
Bradshaw, M. A., Takoma Park, Md.
Brown, B. E., Bureau of Plant Industry, Washington, D. C.
Bubb, John C., 719 Ninth St., N. E., Washington, D. C.
Buchanan, Miss Ruth, Bureau of Chemistry, Washington, D. C.
Burritt, Loren, U. S. Internal Revenue, Washington, D. C.
Burroughs, Lillian C., State Department of Health, Baltimore, Md.

Capen, Miss R. G., Bureau of Chemistry, Washington, D. C.
Carpenter, F. B., Virginia-Carolina Chemical Co., Richmond, Va.
Carroll, John S., Potash Syndicate, New York, N. Y.
Casey, F. W., Bureau of Internal Revenue, Washington, D. C.
Cathcart, P. H., Ballston, Va.
Charlton, R. C., American Agricultural Chemical Co., Baltimore, Md.

Chesnut, V. K., Bureau of Chemistry, Washington, D. C.
Clark, A. W., Agricultural Experiment Station, Geneva, N. Y.
Clarke, W. F., Bureau of Chemistry, Washington, D. C.
Clevenger, J. F., Bureau of Chemistry, Washington, D. C.
Coe, M. R., Bureau of Chemistry, Washington, D. C.
Collins, Miss E. W., Federal Relations Bureau, Inc., Washington, D. C.
Conrad, C. M., University of Maryland, College Park, Md.
Cook, F. C., Bureau of Chemistry, Washington, D. C.
Craig, R. S., City Health Department, Baltimore, Md.
Crawford, C. W., Bureau of Chemistry, Washington, D. C.
Crooke, H. L., Box 1064, Raleigh, N. C.
Cummings, J. A., U. S. Food and Drug Inspection Station, New York, N. Y.
Custis, H. H., Bureau of Animal Industry, Washington, D. C.

Dachnowski, A. P., Bureau of Plant Industry, Washington, D. C.
Dallas, Miss M. A., Bureau of Chemistry, Washington, D. C.
Davidson, Mrs. E. W., 2345 Ashmead Place, Washington, D. C.
Davidson, J., Bureau of Chemistry, Washington, D. C.
Davis, Miss C. M., Bureau of Chemistry, Washington, D. C.
Davis, R. O. E., Bureau of Soils, Washington, D. C.
Davis, Watson, 1115 Connecticut Avenue, N. W., Washington, D. C.
Dawson, P. R., Bureau of Plant Industry, Washington, D. C.
Deemer, R. B., Bureau of Plant Industry, Washington, D. C.
DeLawder, J. L., Bureau of Internal Revenue, Washington, D. C.
Dewar, E. S., Department of Agriculture, Raleigh, N. C.
Doolittle, R. E., Transportation Building, Chicago, Ill.
Doran, J. M., Bureau of Internal Revenue, Washington, D. C.
Dunbar, P. B., Bureau of Chemistry, Washington, D. C.
Dunlap, F. L., 1457 Monadnock Block, Chicago, Ill.

Easterwood, H. W., Bureau of Soils, Washington, D. C.
Edmonds, H. G., Bureau of Internal Revenue, Washington, D. C.
Edmonds, M. J., 1358 Shepherd St., Washington, D. C.
Ellett, W. B., Blacksburg, Va.
Ellis, J. F., Bureau of Chemistry, Washington, D. C.
Ellis, N. R., Bureau of Animal Industry, Washington, D. C.
Emery, W. O., Bureau of Chemistry, Washington, D. C.
Esty, J. R., 623 Varnum St., N. W., Washington, D. C.
Ethier, L. S., Bureau of Chemistry, Washington, D. C.
Evenson, O. L., Bureau of Chemistry, Washington, D. C.

Fellows, H. C., Bureau of Agricultural Economics, Washington, D. C.
Ferguson, J. J., Swift and Company, Chicago, Ill.
Fippin, E. O., 407 Star Building, Washington, D. C.
Fiske, A. H., Rumford Chemical Works, Providence, R. I.
Fitz, L. A., Fleischmann Co., New Rochelle, N. Y.
Fleming, R. S., Merrell-Soule Co., Syracuse, N. Y.
Flenner, A. L., University of Maryland, College Park, Md.
Fletcher, C. C., Bureau of Soils, Washington, D. C.
Forbes, D. R., National Preservers Association, Washington, D. C.
Fox, Edward J., Bureau of Soils, Washington, D. C.
Fraps, G. S., Agricultural Experiment Station, College Station, Tex.
French, D. M., American Agricultural Chemical Co., Alexandria, Va.
Frey, R. W., Bureau of Chemistry, Washington, D. C.

Frere, F. J., 1817 Kalorama Road, Washington, D. C.
Frisbie, W. S., Bureau of Chemistry, Washington, D. C.
Fuller, F. D., Agricultural Experiment Station, College Station, Tex.

Gardiner, R. F., Bureau of Soils, Washington, D. C.
Gascoyne, W. J., 27 South Gay Street, Baltimore, Md.
Gensler, H. E., Bureau of Chemistry, Harrisburg, Pa.
Gephart, F. C., 23 E. 31st St., New York, N. Y.
Gersdorff, C. E. F., Bureau of Chemistry, Washington, D. C.
Gersdorff, W. A., Department of Agriculture, Washington, D. C.
Gibson, A. L., Ontario Agricultural College, Guelph, Canada.
Glycart, C. K., Transportation Building, Chicago, Ill.
Goodrich, C. E., Bureau of Chemistry, Washington, D. C.
Gordon, N. E., Agricultural Experiment Station, College Park, Md.
Gowen, P. L., Bureau of Chemistry, Washington, D. C.
Graham, J. J. T., Bureau of Chemistry, Washington, D. C.
Grayson, Miss M. C., Bureau of Chemistry, Washington, D. C.
Griffin, E. L., Bureau of Chemistry, Washington, D. C.
Grotlisch, V. E., Bureau of Chemistry, Washington, D. C.
Guthrie, C. P., Fargo, N. D.

Haigh, L. D., Missouri Experiment Station, Columbia, Mo.
Haller, H. L. J., Bureau of Chemistry, Washington, D. C.
Hallam, H. C., Hibbs Building, Washington, D. C.
Halvorson, H. A., Old Capitol Building, St. Paul, Minn.
Hand, W. F., Agricultural and Mechanical College, Agricultural College, Miss.
Hanks, A. K., Spencer Lens Company, New York, N. Y.
Hann, R. M., Bureau of Chemistry, Washington, D. C.
Hanson, Alfred W., Transportation Building, Chicago, Ill.
Hanson, H. H., State Board of Health, Dover, Del.
Hart, B. R., Department of Commerce, Washington, D. C.
Hart, F. L., Bureau of Chemistry, Washington, D. C.
Hartwell, B. L., Agricultural Experiment Station, Kingston, R. I.
Haskins, H. D., Agricultural Experiment Station, Amherst, Mass.
Hasselbring, H., Department of Agriculture, Washington, D. C.
Hayes, J. F., Department of Agriculture, Washington, D. C.
Haywood, J. K., Bureau of Chemistry, Washington, D. C
Hazen, William, Bureau of Soils, Washington, D. C.
Heath, W. H., Bureau of Chemistry, Washington, D. C.
Himmler, L. W., Bureau of Animal Industry, Washington, D. C.
Hoffman, C., 132 Bella Vista Ave., Tuckahoe, N. Y.
Holman, H. P., Bureau of Chemistry, Washington, D. C.
Holmes, A. A., 233 Broadway, New York, N. Y.
Holmes, M. G., Northwood, N. H.
Holmes, R. S., Bureau of Soils, Washington, D. C.
Hoover, G. W., Transportation Building, Chicago, Ill.
Horne, W. D., Yonkers, N. Y.
Hortvet, Julius, State Dairy and Food Commission, St. Paul, Minn.
Houghton, H. W., Hygienic Laboratory, Washington, D. C.
Howard, B. J., Bureau of Chemistry, Washington, D. C.
Howe, Harold, University of Maryland, College Park, Md.
Howe, H. E., 810 18th St., N. W., Washington, D. C.
Huffard, C. L., College Park, Md.
Huffington, Jesse M., University of Maryland, College Park, Md.

Hunter, A. C., Bureau of Chemistry, Washington, D. C.
Hurd, W. D., 819 Southern Building, Washington, D. C.
Huston, H. A., 42 Broadway, New York, N. Y.

Jackson, R. F., Bureau of Standards, Washington, D. C.
Jacob, K. D., Bureau of Soils, Washington, D. C.
Jacobs, B. R., 2026 Pennsylvania Avenue, N. W., Washington, D. C.
Jamieson, G. S., Bureau of Chemistry, Washington, D. C.
Jarrell, T. D., Bureau of Chemistry, Washington, D. C.
Jenkins, L. J., Bureau of Chemistry, Washington, D. C.
Jensen, O. F., 819 Southern Building, Washington, D. C.
Jinkins, R., Bureau of Chemistry, Washington, D. C.
Johnson, J. M., Hygienic Laboratory, Washington, D. C.
Jones, D. B., Bureau of Chemistry, Washington, D. C.
Jones, R. M., Bureau of Soils, Washington, D. C.
Jongeward, M., 504 Tulip Ave., Takoma, D. C.

Kebler, L. F., Bureau of Chemistry, Washington, D. C.
Keenan, G. L., Bureau of Chemistry, Washington, D. C.
Keister, J. T., Bureau of Chemistry, Washington, D. C.
Kellogg, J. W., Department of Agriculture, Harrisburg, Pa.
Kerr, A. P., Agricultural Experiment Station, Baton Rouge, La.
Kerr, R. H., Bureau of Animal Industry, Washington, D. C.
King, J. F., State Capitol, Atlanta, Ga.
Kirby, W. E., New York, N. Y.
Koser, S. A., Bureau of Chemistry, Washington, D. C.
Kraybill, H. R., Agricultural Experiment Station, Durham, N. H.
Kunst, F. B., Agricultural Experiment Station, Morgantown, W. Va.

Ladd, E. F., Fargo, N. D.
Lapp, Miss M. E., Bureau of Chemistry, Washington, D. C.
Law, T. C., Law and Company, Atlanta, Ga.
LeClerc, J. A., Department of Commerce, Washington, D. C.
LeFevre, Edwin, Bureau of Chemistry, Washington, D. C.
Leighty, W. R., Bureau of Plant Industry, Washington, D. C.
Leith, T. B., Department of Agriculture, Morgantown, W. Va.
Leonard, C. S., Hygienic Laboratory, Washington, D. C.
Lepper, H. A., Bureau of Chemistry, Washington, D. C.
Lichtenwalner, D. C., University of Maryland, College Park, Md.
Linder, W. V., Bureau of Internal Revenue, Washington, D. C.
Linton, F. B., Bureau of Chemistry, Washington, D. C.
Lodge, F. S., Armour Fertilizer Works, Chicago, Ill.
Loomis, H. M., National Canners Association, Washington, D. C.
Lynch, W. D., Bureau of Chemistry, Washington, D. C.
Lythgoe, H. C., Department of Public Health, Boston, Mass.

MacIntire, W. H., University of Tennessee, Knoxville, Tenn.
Magruder, E. W., F. S. Royster Guano Company, Norfolk, Va.
Manross, Miss L. M., Hygienic Laboratory, Washington, D. C.
Markovitz, L. N., Bureau of Chemistry, Washington, D. C.
Marshall, W. K., Bureau of Agricultural Economics, Washington, D. C.
Martin, J. B., 1408 Shepherd Street, N. W., Washington, D. C.
Mayer, O. F., H. T. Heinz Co., Pittsburgh, Pa.
McCall, A. G., Agricultural Experiment Station, College Park, Md.
McDonnell, C. C., Bureau of Chemistry, Washington, D. C.

McDonnell, H. B., Agricultural Experiment Station, College Park, Md.
McHargue, J. S., Agricultural Experiment Station, Lexington, Ky.
McMillin, H. R., Bureau of Animal Industry, Washington, D. C.
Mehring, A. L., Bureau of Soils, Washington, D. C.
Mehurin, R. M., Bureau of Animal Industry, Washington, D. C.
Miller, G. E., Bureau of Chemistry, Washington, D. C.
Milne, Miss E. L., Bureau of Chemistry, Washington, D. C.
Miner, C. S., The Miner Laboratories, Chicago, Ill.
Mitchell, A. S., Bureau of Chemistry, Washington, D. C.
Mix, Miss A. E., Bureau of Chemistry, Washington, D. C.
Moore, Miss M. D., Bureau of Chemistry, Washington, D. C.
Morawski, A. L., Bureau of Internal Revenue, Washington, D. C.
Morison, C. B., 1133 Fullerton Ave., Chicago, Ill.
Morton, J. K., Bureau of Chemistry, Washington, D. C.
Moulton, S. C., Health Department, Washington, D. C.
Mount, J. M., Williams & Wilkins Company, Baltimore, Md.
Munch, J. C., Bureau of Chemistry, Washington, D. C.
Murray, A. G., Bureau of Chemistry, Washington, D. C.

Nelson, E. K., Bureau of Chemistry, Washington, D. C.
Nordeman, Miss A. M., Department of Agriculture, Washington, D. C.
Nothstine, A. C., 946 Shepherd St., N. W., Washington, D. C.

O'Brien, Miss A. B., Bureau of Chemistry, Washington, D. C.
Oswald, Carl L., 1004 Eye St., N. W., Washington, D. C.

Palkin, S., 1217 N St., N. W., Washington, D. C.
Pappe, T. F., Bureau of Chemistry, Washington, D. C.
Parkins, J. H., F. S. Royster Guano Company, Norfolk, Va.
Parkinson, Miss N. A., 1216 Delafield Place, N. W., Washington, D. C.
Patten, A. J., Agricultural Experiment Station, E. Lansing, Mich.
Patterson, H. J., Agricultural Experiment Station, College Park, Md.
Paul, A. E., 411 Post Office Building, Cincinnati, Ohio.
Pease, Miss V. A., Bureau of Chemistry, Washington, D. C.
Peeples, W. M., Baugh Chemical Company, Baltimore, Md.
Phelps, I. K., Bureau of Chemistry, Washington, D. C.
Phillips, M., Bureau of Chemistry, Washington, D. C.
Phillips, S., Bureau of Chemistry, Washington, D. C.
Pingree, M. H., American Agricultural Chemical Company, Baltimore, Md.
Pope, W. B., 3171 18th St., N. W., Washington, D. C.
Power, F. B., Bureau of Chemistry, Washington, D. C.
Powick, W. C., Bureau of Animal Industry, Washington, D. C.
Probey, T. F., Hygienic Laboratory, Washington, D. C.
Proulx, E. G., Agricultural Experiment Station, Lafayette, Ind.
Randall, W. W., Department of Health, Baltimore, Md.
Read, Miss E. A., Bureau of Chemistry, Washington, D. C.
Redfield, H. W., Bureau of Chemistry, New York City, N. Y.
Reed, J. B., Bureau of Chemistry, Washington, D. C.
Reid, F. R., Bureau of Soils, Washington, D. C.
Reid, W. D., Swift and Company, Baltimore, Md.
Reindollar, W. F., Department of Health, Baltimore, Md.
Remsburg, C. G., Hygienic Laboratory, Washington, D. C.
Rice, E. L., 316 Machinist Building, Washington, D. C.
Richardson, W. D., Swift and Company, Chicago, Ill.

Rider, Miss A. B., 307 C Street, N. W., Washington, D. C.
Riffenburg, H. B., U. S. Geological Survey, Washington, D. C.
Riley, A. A., U. S. Internal Revenue, Washington, D. C.
Riley, H. N., H. J. Heinz Co., Pittsburgh, Pa.
Riley, J. G., Bureau of Internal Revenue, Washington, D. C.
Roark, R. C., General Chemical Company, Baltimore, Md.
Roberts, O. S., Lafayette, Ind.
Robey, V. C. K., Bureau of Internal Revenue, Washington, D. C.
Robinson, C. S., Agricultural Experiment Station, E. Lansing, Mich.
Robinson, W. V., Bureau of Soils, Washington, D. C.
Ross, B. B., Polytechnic Institute, Auburn, Ala.
Ross, W. H., Bureau of Soils, Washington, D. C.
Ruprecht, R. W., Experiment Station, Gainsville, Fla.
Russ, R. F., 32 Franklin St., N. E., Washington, D. C.
Rutledge, Miss R. L., Bureau of Chemistry, Washington, D. C.
Ryan, R. L., Bureau of Internal Revenue, Washington, D C.

Sample, J. W., Nashville, Tenn.
Schertz, F. M., Bureau of Soils, Washington, D. C.
Schlupp, W. F., Experiment Station, Potchefstroom, S. Africa.
Schneller, M. A., 821 Virginia Ave., Washington, D. C.
Schulze, W. H., Department of Health, Baltimore, Md.
Schwartze, E. W., Bureau of Chemistry, Washington, D. C.
Schwarz, R., 113 Hudson Street, New York City, N. Y.
Scott, R. D., Department of Health, Columbus, O.
Sebring, B. W., Department of Agriculture, Columbus, O.
Seidenberg, Armin, Department of Health, New York, N. Y.
Shaver, A., 919 L Street, N. W., Washington, D. C.
Shovey, E. C., Bureau of Plant Industry, Washington, D. C.
Shrader, J. H., Department of Health, Baltimore, Md.
Shulenberger, F. W., Eimer and Amend, New York City, N. Y.
Sigler, P. S., 2721 Connecticut Avenue, N. W., Washington, D. C.
Skinner, J. J., Bureau of Plant Industry, Washington, D. C.
Skinner, Miss L. A., Bureau of Chemistry, Washington, D. C.
Skinner, W. W., Bureau of Chemistry, Washington, D. C.
Slipher, J. A., 2803 13th Street, N. E., Washington, D. C.
Smith, A. M., University of Maryland, College Park, Md.
Smith, C. M., Bureau of Chemistry, Washington D. C.
Smith, C. R., Bureau of Chemistry, Washington, D. C.
Smith, J. G., Bureau of Soils, Washington, D. C.
Smith, Miss J. K., Bureau of Chemistry, Washington, D. C.
Smith, Miss K. A., Bureau of Chemistry, Washington, D. C.
Smith, Miss S. L., States Relations Service, Washington, D. C.
Smith, W. C., Bureau of Chemistry, Washington, D. C.
Smither, F. W., Bureau of Standards, Washington, D. C.
Snyder, E. F., 1827 Monroe St., N. W., Washington, D. C.
Snyder, H., 1800 Summit Ave., Minneapolis, Minn.
Sorber, D. G., Bureau of Animal Industry, Washington, D. C.
Spencer, G. C., Bureau of Chemistry, Washington, D. C.
Stengel, A., Bureau of Chemistry, Washington, D. C.
Stephenson, C. H., Bureau of Chemistry, Washington, D. C.
Sterling, W. F., Bureau of Chemistry, Washington, D. C.
Stevenson, A. E., National Canners Association, Washington, D. C.

Stokes, W. E., Royal Baking Powder Co., New York, N. Y.
Strowd, W. H., Department of Agriculture, Madison, Wis.
Swicker, V. C., 713 Princeton Place, Washington, D. C.

Taylor, A. E., Bureau of Chemistry, Washington, D. C.
Thatcher, A. S., Loose-Wiles Biscuit Company, Long Island City, N. Y.
Thomas, Mrs. A., 1338 Vermont Ave., N. W., Washington, D. C.
Thomas, Walter, State College, Pa.
Thompson, E. C., The Borden Company, New York City, N. Y.
Thompson, H. L., Empire Laboratory Supply Company, New York, N. Y.
Thompson, J. W., Hygienic Laboratory, Washington, D. C.
Thornton, E. W., R. B. Davis Co., Hoboken, N. J.
Toll, J. D., 1010 Arch Street, Philadelphia, Pa
Tonkin, W. H., Bureau of Chemistry, Washington, D. C.
Tracewell, C. E., Evening Star, Washington, D. C.
Trowbridge, P. F., Agricultural Experiment Station, Agricultural College, N. D.
Turner, W. A., Riverdale, Md.
Turrentine, J. W., Bureau of Soils, Washington, D. C.

Ullrich, Miss J. R., 25 Beaver Street, New York, N. Y.

Valaer, Peter, Jr., Bureau of Internal Revenue, Washington, D. C.
Van Horn, R. C., Western Maryland Dairy, Baltimore, Md.
Van Norman, H. E., 426 Star Building, Washington, D. C.
Van Wormer, L. H., College Park, Md.
Veitch, F. P., Bureau of Chemistry, Washington, D. C.
Vollertsen, J. J., Morris and Company, Chicago, Ill.

Waggaman, W. H., Bureau of Soils, Washington, D. C.
Walker, P. H., Bureau of Standards, Washington, D. C.
Walls, H. R., University of Maryland, College Park, Md.
Walton, G. P., Bureau of Soils, Washington, D. C.
Weber, F. C., Bureau of Chemistry, Washington, D. C.
Weems, J. B., Department of Agriculture, Richmond, Va.
Wherry, E. T., Bureau of Chemistry, Washington, D. C.
White, W. R., Department of Agriculture, Ottawa, Canada.
Whitney, C. F., Burlington, Vt.
Wilcox, E. L., 10 - 10th St., N. E., Washington, D. C.
Wiley, H. W., 1120 Woodward Building, Washington, D. C.
Wiley, S. W., Wiley and Company, Inc., Baltimore, Md.
Williams, C. C., National Canners Association, Washington, D. C.
Wilson, Miss A., Bureau of Chemistry, Washington, D C.
Wilson, J. B., Bureau of Chemistry, Washington, D. C.
Wilson, S. H., Department of Agriculture, Atlanta, Ga.
Wilson, S. M., Baugh Chemical Company, Baltimore, Md.
Winant, H. B., Agricultural Experiment Station, College Park, Md.
Wolf, M. G., 600 W. 187th St., New York City, N. Y.
Wrenn, J. E., Department of Commerce, Washington, D. C.
Wright, C. D., Bureau of Chemistry, Washington, D. C.
Wright, L E., Experimental Farm, Ottawa, Canada.
Wright, P. A., Department of Agriculture, Washington, D. C.

Young, J. L., 2517 Wisconsin Ave., Washington, D. C.

Zerban, F. W., Penick and Ford, Ltd., Inc., New Orleans, La.

PRESIDENT'S ADDRESS[1].

THE OPPORTUNITIES AND RESPONSIBILITIES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

By F. P. Veitch (Bureau of Chemistry, Washington, D. C.).

It has been my privilege to listen to the addresses before this association for the past thirty years, and some of these have dealt with the subject matter of my brief talk on "The Opportunities and Responsibilities of the Association of Official Agricultural Chemists". I can not hope to say anything that is new nor can I hope to present the matter as well as it has been done by others. Nevertheless, convinced that the subject is a live one at this time, I trust that I may be able to redirect attention to it to some purpose.

The objects of the association, as stated by the constitution, are two: "To secure uniformity and accuracy in the methods, results and modes of statement of analysis of fertilizers, soils, cattle foods, dairy products, and other materials connected with agricultural industry"; and, "to afford opportunity for the discussion of matters of interest to agricultural chemists". Proceeding with these broad subjects, this association was, so far as I know, the first to introduce and to develop effectively the collaborative study of methods and of men. It has done well in these particulars. Other organizations, growing out of it or organized more recently, have followed more or less in the footsteps of this association, but it is fair to say, I think, that none of them has given that thorough, careful and judicial study to analytical methods that has characterized the Association of Official Agricultural Chemists, and which has won for it the respect and confidence not only of the farmer but of those industries that cater to his needs. Unquestionably this association has developed the most accurate, reliable and simple methods for the analysis of those materials with which it deals. As important as this is to all agricultural work, it is, to my mind, far less important than what has been developed therefrom—incidentally probably—and that is the training of a body of real analytical chemists, men trained in methods of investigation, who can do a reasonable volume of reliable work. These results have followed not merely from the routine participation in the collaborative work of the association, but, I am persuaded, primarily from the full and vigorous discussions thereon, which took place particularly in the earlier years of the association.

These things being true, why has it been deemed necessary or even desirable for other organizations to repeat and duplicate much of the

[1] Presented Thursday morning, November 16, as special order of business for 11 o'clock.

work done by this association? Why must three, or perhaps more, other organizations investigate the determination of the iodine numbers of oils? Are our methods for the determination of nitrogen, or phosphoric acid, or sucrose, or carbon dioxide, or magnesium oxide, or fats and oils, or for the preparation of reagents, for example, so inadequate or so faultily stated that these methods, developed from collaborative work of from ten to thirty chemists over a period of twenty years or more, can be made more accurate and rapid and can be more clearly stated as the result of the work of a year or two by others? Why is it necessary for these organizations to do more than adopt these methods, which are the outcome of many years of careful, thorough and impartial cooperative effort? What can be done to stop this waste of time and effort and the doubt and conflict that result from the use of different methods?

We can not escape the larger share of the responsibility for these conditions. We have not been active enough either individually or as an organization in keeping informed as to the activities of others, or in cooperating in, and—may I say—shaping, the activities of these organizations and in saving them needless work. Having in mind my own shortcomings during the year it has been my honor to serve as the head of this organization. I am constrained to think that the officers of the association have given little thought to this phase of the association's duties.

As the pioneer organization, this association should properly extend its efforts to eliminate this waste of time and effort and to further accuracy and uniformity in methods of examination. I believe that each of us should bring to the attention of the secretary of the association any proposed outside activity within the field of this association of which he learns and, if through personal acquaintance it is possible, to endeavor to coordinate such work with the work of this association. The secretary should bring such matters before the Executive Committee, call the attention of the other organizations to our work and methods, and offer the assistance of our association. The Executive Committee, if requested to do so, should have the authority to designate a small committee to cooperate with the other organizations to promote uniformity and eliminate useless efforts. Thus, in a larger way, it seems to me, we would be carrying out the objects of the association and extend its influence and usefulness.

Discussion is the life blood of organizations; it denotes interest in and knowledge of the subject; it promotes work, expands knowledge and helps to make capable, efficient men. Those of us who recall the discussions of the earlier meetings realize fully how stimulating, informing and helpful they were. We went back to our desks with increased interest and refreshed minds, and took up the burdens of the day with

renewed vigor, derived almost wholly, I venture to assert, from the discussions—formal and informal—that took place, rather than directly from the reports and papers that were presented. To my mind it is an indefensible waste of time and effort for any body of men to gather simply to listen to the reading of papers, to pass a few resolutions and elect officers. The papers can be read when published, while the resolutions and elections are useless if they are not the outgrowth of the meeting of men's minds.

I have watched with much concern the flaring up and the dying down of interest and discussions in a half-dozen associations and societies. We are not alone in this condition, but it behooves us to correct it now. You will think of many ways in which this can be done and I may mention a few.

Here, too, the officers of the association should be active, more especially in preparing to insure full cooperation and attendance and to present a well-thought-out, attractive program. Success can not be expected to attend efforts limited to a week or two before the annual meetings. The work should be clear cut and comprehensive, but not burdensome. The institutions participating should have the collaborative work done promptly and well and reported to the referee in ample time for him to prepare a clear, informing and brief report. Moreover, at least one representative from each organization should attend the annual meetings. We are not developing methods only but we are training our force for better things if there can be better things than doing well the duty before us.

Reports and papers should not be longer than necessary and should be prepared to bring out clearly the points presented. Tables of results passed around develop and hold interest. Details should be left to the discussion. The program should be arranged to give unlimited time for discussion, even though it require an additional day. We should give this work our close attention; we are here for a purpose. Each of us, and especially if an older member, should be prepared to open the discussion on any subject that is within our knowledge, either to contribute to or to receive some benefit from the work.

Finally, I believe we should return to the old practice of printing a full report of the proceedings, including the useful discussions. If we can do these things, we will have taken a long step toward the revival of that productive interest of earlier days, the passing of which has concerned us all.

While we may confidently believe that our methods are the best in existence, sight must not be lost of the fact that they can be improved or that their usefulness can be increased and extended. The arbitrary method for the determination of available phosphoric acid in fertilizers has not been modified fundamentally in thirty years, although it is

known that it is not based on unimpeachable evidence. The availability of phosphoric acid in basic slag has long been a problem to which the association apparently is now finding a satisfactory solution. Should agriculture recognize potash in fertilizers other than in its water-soluble forms? Nitrogen is the most expensive and possibly in general the most important plant food which the farmer buys. It exists in many forms of widely differing availability. Through the increasing and to-be-encouraged utilization of waste, nitrogenous fertilizer materials are being added to almost daily. Are we keeping the farmer informed as fully as we can and should concerning the presence and value of these various forms in the fertilizers which he buys?

It has been 21 years since Dr. C. G. Hopkins and his associates, and also the speaker, proposed before this association quantitative methods for determining the "acidity" or "lime requirement" of soils, while even earlier Wheeler and Hartwell had been investigating the subject. Other methods have long since been suggested and some of these are in use. For the past 10 years the literature has been flooded with undergraduate and graduate efforts on this vital economic problem but to date this association has no method for determining the "lime requirement" of soil.

Is any man here confident that he can get agreeing results on moisture in a complex organic material, on two successive days? The methods for determining tannin have always been known to give results that are too high—how much too high we can not even guess. Recently we have found in my own laboratory that the quantity of samples employed, though within the limits stated in the method, is responsible for marked differences in the iodine number of rosin. If this is found to be true of other fats, oils and resins, we have a partial explanation of differences in results on iodine number and must needs revise our method accordingly. Numerous other instances of pressing need for better methods will occur to you, and these should be met by greater individual and collaborative activity on the part of our members.

Most of the matters I have mentioned are of long standing. The efforts that have been given to them have not led to material advances. We need to go at these and similar problems more earnestly and bring to bear upon them the more recent as well as the older knowledge. Nothing is of greater fundamental importance than the maintenance of the fertility of the land, involved in which is definite knowledge of the availability of plant foods and of the factors which determine it. I venture to suggest that the longest step that this association can take now toward the solution of these and other dormant problems is to appoint committees of one to study thoroughly a number of them, summarize the work heretofore done and make definite recommendations for further work. These reports should be printed in *The Journal*

and should be in the hands of the members before the next annual meeting in order that those interested might familiarize themselves with and be prepared to discuss them at that time.

What could be more helpful now, for example, than an extended review of the availability of the different forms of phosphoric acid and different phosphates by Dr. Hartwell, discussed by Dr. Thorne, Dr. Haskins, Dr. Patterson, Dr. Wheeler, Mr. Williams, and others, or a review, by Dr. Lipman of New Jersey, of the different forms of nitrogen, with discussion by Dr. Hartwell, Dr. Blair and Dr. Thorne? And so with these other big fundamental problems that have held the advance of the association for many years. I invite your earnest consideration of the suggestion that we mark time for a year in at least some of our collaborative work that we may take stock and survey the field through these expert summaries and discussions in order that our attack may be intelligently concentrated on the crucial points in some of these baffling problems. Personally I am fully convinced that much more is to be gained in this way just now than by any other procedure.

One other thought and I am through. Years ago a distinguished member of this association remarked that no line of agricultural work progresses far before it is necessary to call in the chemist. This should be a more generally recognized fact. Take chemistry out of biology or nutrition and little but a name is left. Forget and abandon today's chemical knowledge in agriculture, and industry and civilization drop back 2000 years, because even in those days they were recognizing the rudiments of applied chemistry. In peace and in war it plays its major part.

This being true, have we individually and as an association lived up to our opportunities—have we met our responsibilities? Have we placed assertively and confidently at the service of the people, especially at the service of agriculture, that training, experience and knowledge that is ours? Have we assumed the commanding, directing position in public affairs, in research organizations and in scientific police work that the fundamental importance of chemistry imposes upon us? Do we insist that the burden of proof shall be assumed by the new and untried rather than by the old and proved? Do we employ unceasingly that infallible weapon "publicity" in the service of the people?

There exists in each state an agricultural college—a capable, impartial, experienced scientific organization—which can conduct research or function to protect the people. It is, I believe, our duty as an association and as individuals to see that these facts are fully known whenever it is proposed to conduct research or enact laws against frauds in material, because such work can be most effectively and economically done by these organizations. So many concrete things are worth doing that the tendency to needless expansion and duplication is difficult to foresee or

to check. Both are so wasteful of the people's funds, of time and effort that they should be guarded against at all times.

It seems to me, then, that in addition to the well established work on methods and their application upon which we have long been engaged the association can and should take a larger directing part in all scientific service relating to agriculture. When service, private or public, involving chemistry is to be performed, let us get from the chemist all that he has to give.

CHANGE IN ORDER OF PUBLICATION.

The order of publishing the committee reports will be reversed this year; that is, they will be published at the beginning of the proceedings rather than in their chronological order at the end, as has formerly been done. In this way the referees and associate referees will have readily available the matter for beginning the year's work.

THIRD DAY.

FRIDAY—MORNING SESSION.

REPORT OF THE COMMITTEE ON EDITING METHODS OF ANALYSIS.

The work of your Committee on Editing Methods of Analysis has not been very extensive during the past year. You will recall that the committee in its report at the 1921 meeting called attention to the necessity for a revision of the methods in the near future and invited suggestions for ways and means of improving the present *Book of Methods* when such a revision was made. No suggestions of this character have been received. As the result of a recent conference with the Board of Editors of *The Journal* and another with the Board of Directors of the association, it has been decided to begin at once a revision of the official and tentative methods of analysis in order that the work may be completed soon after the next meeting, which will be the fifth since the present book was issued. It is planned to carry out the greater part of the work during the present year so that immediately after the close of the 1923 meeting the additions and changes made at that meeting can be incorporated and the new *Book of Methods* made ready for distribution by July 1, 1924. This will make the revision occur at the five-year interval which the association appeared to favor at the time the last revision was made. Your committee plans to retain the present form of the *Book of Methods*, the revision to consist principally in the deletion of methods which have been dropped and the incorporation of new methods and of additions and changes which have been made to the methods. We wish, therefore, to renew our request of last year for suggestions for improving the form or arrangement of the methods whereby they may be made more useful or convenient, and for reports of any errors that have been noted in the present edition. The co-operation of all referees and associate referees and of the sub-committees

on recommendations of referees is most urgently requested, particularly for the purpose of bringing before the association at the meeting next year all methods, changes in methods and deletions on which final action can be taken so that they may be incorporated in the revised edition of the *Book of Methods.* Every referee and associate referee is urged to study carefully the chapter of the methods or the portion of the chapter of methods with which he is directly concerned for the purpose of recommending the deletions and changes which should be made to make the chapters as complete and up-to-date as it is possible to make them. Your committee will undoubtedly call upon the referees and associate referees for assistance in editing the methods.

There was referred to your committee, at the last meeting of the association, the following resolution from Sub-committee C on Recommendations of Referees:

Methods for the macroscopical and microscopical identification of certain drugs have been reported with the results of collaborative study thereon. Inasmuch as such methods represent a radical departure from the policy of this association, it is recommended that these be referred to the Committee on Editing Methods of Analysis for consideration before any action is taken.

A consideration of the methods referred to showed that they consisted of statements of the macroscopical and microscopical characteristics of the various parts of the plant as compared with those of the substitutes found. These differentiations are based entirely upon the botanical structure of the plant, and it is believed that these methods belong more properly in the United States Pharmacopœia, or a text book dealing with the botanical structure of medicinal plants. It is therefore the opinion of your committee that these botanical descriptions of distinction should not be included in the official and tentative methods of analysis of the association.

During the past year the chairman of your committee was requested by the Chairman of the Board of Editors of *The Journal* to prepare, in a form suitable for separate publication, the official and tentative methods of the association for the analysis of milk, in order that these methods might be considered by the Board of Editors, the Executive Committee and the association itself in connection with a request received from the Secretary of the American Public Health Association for a joint publication of the methods of the two associations for the examination of milk. As is generally known, the American Public Health Association has published for a number of years a pamphlet containing the bacteriological methods adopted by the Laboratory Section of that association for the examination of milk. There have been three editions of this pamphlet. A fourth edition is now being prepared in which the Public Health Association desires to incorporate the necessary chemical methods for the examination of milk. Consequently this request for

a joint publication of the two sets of methods has been made. The proposition appealed to the members of your Committee on Editing Methods of Analysis, provided the identity of the chemical methods as the methods of the Association of Official Agricultural Chemists was maintained. The methods for the analysis of milk as printed in Chapter XXI of the *Book of Methods*, together with the additions and changes made subsequent to November 1, 1919, were accordingly prepared for publication in separate form by incorporating the text of other chapters where cross references appear. This set of methods has been submitted to the Laboratory Section of the American Public Health Association, which section has agreed to accept same. The methods have also been submitted to the Board of Editors of *The Journal*, and the advisability of joining the American Public Health Association in the joint publication of the milk methods has been discussed with the Board of Editors and the Executive Committee of the association, both of which have approved the plan.

Your committee therefore recommends that the association approve the plan presented by the Secretary of the American Public Health Association for a joint publication of the bacteriological and chemical methods of the two associations for the examination of milk on condition that the identity of the chemical methods as the A. O. A. C. methods be retained in such a publication, and that the Board of Editors be authorized to attend to the details of such a publication.

The attention of your committee has been called to an error in the method for the determination of starch by the diastase method[1], by C. P. Walton of the Bureau of Chemistry. Lines 11 and 12, page 96, direct the analyst to correct the weight of reduced copper by that obtained on a blank of the same volume. This correction should be made upon the equivalent weight of dextrose obtained by that determined upon an equal volume of the malt blank as the weight of dextrose is not in direct proportion to the weight of reduced copper obtained. This is clearly indicated under "Reagent", page 95, but as the two sections now read there is an apparent contradiction in the procedure to be followed. Proper correction will be made in the next revision of the methods.

Your committee has prepared a compilation of the changes and additions which were made to the official and tentative methods at the 1921 meeting of the association. This has been done as in former years in order that the members of the association may have grouped together for convenience of reference the additions and changes made from year to year. A brief summary of these additions and changes for the 1921 meeting, attached as a part of this report, shows that of the thirty chap-

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 95, par. 61.

ters of the book fifteen, or one-half, received some additions or changes. No changes or additions were made to the following:

Chapter	*Title*
II	Inorganic Plant Constituents.
IV	Tanning Materials.
V	Leathers.
VIII	Saccharine Products.
IX	Food Preservatives.
X	Coloring Matters in Foods.
XI	Metals in Foods.
XV	Wines.
XVI	Distilled Liquors.
XVII	Beers.
XVIII	Vinegars.
XIX	Flavoring Extracts.
XXVII	Baking Powders and Baking Chemicals.
XXIX	Soils.
XXX	Reference Tables.

The additions and changes which were made are as follows:

CHANGES AND ADDITIONS TO THE METHODS OF ANALYSIS MADE AT THE 1921 MEETING.

I. FERTILIZERS.

(1) The Bartlett method[1] for the determination of boric acid in fertizers and fertilizing materials was adopted as a tentative method for reason of the special adaptation of the method to the analysis of samples relatively high in soluble phosphates or organic matter.

(2) The Ross-Deemer method[2] was adopted as a tentative method for the determination of water-soluble boric acid in fertilizers and fertilizing materials for reason of its special adaptation to the analysis of samples low in soluble phosphates and organic matter relative to the boric acid content.

(3) The present official method[3] for the determination of insoluble phosphoric acid in fertilizers was made an official method for the determination of the insoluble phosphoric acid in precipitated phosphates with the exception that a one-gram charge shall be employed instead of a two-gram charge. (First action as an official method.)

(4) It was further provided in the method for the determination of phosphoric acid in precipitated phosphates that a perforated platinum crucible and suction be employed in the filtration of the citrate solution

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 90.
[2] *Ibid.*, 327.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 4.

after treatment and that a filter paper be employed that will insure a free and rapid filtration without allowing the finely divided particles to pass through. The following papers have been found satisfactory (and there may be others): C. S. & S. No. 597; Whatman No. 2; Whatman No. 1; Munktell's No. 1-F; Munktell's No. 2; and Durieux No. 121. (First action as an official method.)

(5) The tentative Wagner method[1] for the determination of available phosphoric acid in basic slag was made official. (First action as an official method.)

II. INORGANIC PLANT CONSTITUENTS.

A method for the determination of manganese[2] was adopted as an official method. (First action as an official method.)

III. WATERS.

(1) A method for the determination of iodine in the presence of chlorine and bromine[3] was adopted as a tentative method.

(2) The tentative method for reporting results of analysis[4] was deleted and in place thereof the new form suggested by the referee in his report for 1921[5], was adopted as a tentative method.

(3) Methods for the determination in salt[6] of moisture, matters insoluble in water and matters insoluble in acid were adopted as tentative methods.

IV. TANNING MATERIALS.

No additions or changes were made at the 1921 meeting.

V. LEATHERS.

No additions or changes were made at the 1921 meeting.

VI. INSECTICIDES AND FUNGICIDES.

(1) The mercury-thiocyanate method[7] for the determination of zinc oxide in zinc arsenite was adopted as an official method. (First action as an official method.)

(2) The bromate method[8], procedures 1 and 2, for the determination of arsenious oxide in zinc arsenite was adopted as an official method. (Final action.)

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 14.
[2] *J. Assoc. Official Agr. Chemists*, 1921, 4: 393.
[3] *Ibid.*, 1922, 5: 381.
[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 38.
[5] *J. Assoc. Official Agr. Chemists*, 1922, 5: 385.
[6] *Ibid.*, 384.
[7] *Ibid.*, 392.
[8] *Ibid.*, 394.

(3) The official method[1] for the determination of water-soluble arsenic in lead arsenate was made an official method for the determination of water-soluble arsenic in zinc arsenite. (Final action.)

(4) The bromate method[2] for the titration of the acid distillate in the official distillation method for the determination of total arsenic was adopted as an official method. (Final action.)

(5) The bromate method[3], procedures 1 and 2, for the determination of arsenious oxide in calcium arsenate was adopted as an official method. (Final action.)

(6) Two methods, (1)[3] and (2)[4], for the determination of calcium oxide in calcium arsenate were adopted as official methods. (First action on both methods as official methods.)

(7) Under the heading, "General Procedure for the Analysis of a Product Containing Arsenic, Antimony, Lead, Copper, Zinc, Iron, Calcium, Magnesium, etc.", methods[5] for the determination of lead oxide and copper were adopted as official methods. (Final action.)

(8) Under the heading, "General Procedure for the Analysis of a Product Containing Arsenic, Antimony, Lead, Copper, Zinc, Iron, Calcium, Magnesium, etc.", an official method[5] was adopted for the determination of zinc oxide. (First action as an official method.)

(9) The zinc oxide-sodium carbonate method[6] for the determination of total arsenic in London purple was adopted as an official method. (Final action.)

(10) The bromate method[7], procedures (**a**) and (**b**), for the determination of arsenious oxide in Paris green was adopted as an official method. (Final action.)

(11) The phrase "Not applicable in the presence of nitrates" was inserted over the present official distillation method for the determination of total arsenic wherever this method appears in the *Book of Methods*.

(12) The distillation method[8], suggested by Graham and Smith for the determination of total arsenic in the presence of nitrates was adopted as a tentative method with a view to its adoption as an official method after it has been tested by cooperative work. (A tentative method—first action as official.)

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 59.
[2] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 394.
[3] *Ibid.*, 395.
[4] *Ibid.*, 396.
[5] *Ibid.*, 398.
[6] *Ibid.*, 1921, **4**: 397.
[7] *Ibid.*, 399.
[8] *Ibid.*, 402.

VII. FOODS AND FEEDING STUFFS.

(1) The official method[1] for the determination of crude fiber was deleted and in place thereof the method[2] proposed by Bidwell and Bopst was adopted as an official method. (First action as an official method.)

(2) The microscopic method[3] for the determination of rice hulls in rice bran was adopted as a tentative method.

VIII. SACCHARINE PRODUCTS.

No additions or changes were made at the 1921 meeting.

IX. FOOD PRESERVATIVES.

No additions or changes were made at the 1921 meeting.

X. COLORING MATTERS IN FOODS.

No additions or changes were made at the 1921 meeting.

XI. METALS IN FOODS.

No additions or changes were made at the 1921 meeting.

XII. FRUITS AND FRUIT PRODUCTS.

(1) A method[4] for the determination of moisture in dried fruits (for dried fruits in general) was adopted as an official method. (First action as an official method.)

(2) A method[4] for the determination of moisture in dried apples was adopted as a tentative method.

XIII. CANNED VEGETABLES.

The wording of the method[5] for the micro-analysis of tomato pulp, catsup, purée, sauce and paste was corrected to make the details of operation clearer and the method as corrected was adopted as official. (First action as an official method.)

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 97.
[2] *J. Assoc. Official Agr. Chemists*, 1922, 5: 421.
[3] *Ibid.*, 77.
[4] *Ibid.*, 6: 48.
[5] *Assoc. Official Agr. Chemists, Methods*, 1920, 164; *J. Assoc. Official Agr. Chemists*, 1922, 6: 49.

XIV. CEREAL FOODS.

A method[1] for the determination of fat in baked cereal products was adopted as a tentative method.

XV. WINES.

No additions or changes were made at the 1921 meeting.

XVI. DISTILLED LIQUORS.

No additions or changes were made at the 1921 meeting.

XVII. BEERS.

No additions or changes were made at the 1921 meeting.

XVIII. VINEGARS.

No additions or changes were made at the 1921 meeting.

XIX. FLAVORING EXTRACTS.

No additions or changes were made at the 1921 meeting.

XX. MEAT AND MEAT PRODUCTS.

(1) A modified method[2] for the determination of nitrates and nitrites calculated as sodium nitrate was adopted as a tentative method in place of the present ferrous chloride method[3] for the determination of nitrates.

(2) The tentative phenoldisulfonic acid method[4] for the determination of nitrates and nitrites calculated to sodium nitrate, was changed by substituting the word "sodium" for "potassium" throughout the text for the purpose of making the comparison with a standard solution of sodium nitrate and expressing the results in terms of sodium nitrate as is the trade practice.

XXI. DAIRY PRODUCTS.

(1) The cryoscopic method[5] for the determination of added water in milk was adopted as an official method. (First action as an official method.)

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 6: 63.
[2] *Ibid.*, 74.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 210.
[4] *Ibid.*, 211.
[5] *J. Assoc. Official Agr. Chemists*, 1922, 5: 173.

(2) The tentative method[1] for the determination of moisture in cheese was modified to provide that either 10–15 grams of sea-sand or 2–3 grams of asbestos be used, and that the sample be dried either in a vacuum or at atmospheric pressure at the boiling point of water.

(3) The Schmidt-Bondzynski method[2] for the determination of fat in cheese was adopted as an official method. (Final action.)

XXII. FATS AND OILS.

(1) The Wijs method[3] for the determination of the iodine absorption number was made official. (Final action.)

(2) An alternative method[4] for the preparation of the Wijs solution was adopted as a part of the official method. (First action as an official method.)

XXIII. SPICES AND OTHER CONDIMENTS.

The tentative method[5] for the determination of volatile oil in mustard seed was made official. (Final action.)

XXIV. CACAO PRODUCTS.

A microscopical method[6] for the determination of cacao shells in cacao and chocolate products was adopted as a tentative method.

XXV. COFFEES.

The Power-Chesnut method[7] for the determination of caffeine in coffee was adopted as an official method. (Final action.)

XXVI. TEA.

(1) The Power-Chesnut method[8] for the determination of caffeine in tea was adopted as an official method. (Final action.)

(2) The Stahlschmidt method[9] for the determination of caffeine in tea was dropped.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 234.
[2] *Ibid.*, 235.
[3] *Ibid.*, 245.
[4] *J. Ind. Eng. Chem.*, 1918, 10: 318.
[5] *Assoc. Official Agr. Chemists, Methods*, 1920, 259.
[6] *J. Assoc. Official Agr. Chemists*, 1922, 5: 257.
[7] *Ibid.*, 271.
[8] *Ibid.*, 290.
[9] *Assoc. Official Agr. Chemists, Methods*, 1920, 274.

(3) The Bailey-Andrew method[1] for the determination of caffeine in tea was adopted as an official method. (First action as an official method.)

XXVII. BAKING POWDERS AND BAKING CHEMICALS.

The modified Chittick method[2] was adopted as a tentative method for the determination of lead in baking powder.

XXVIII. DRUGS.

(1) Under the heading, "Acetylsalicylic Acid", the following additions to the methods for analysis of drugs were made:

(a) A qualitative test[3] for free salicylic acid was adopted as a tentative method.

(b) A method[3] for the quantitative determination of salicylic acid was adopted as a tentative method.

(c) The iodine method[3] for the determination of total salicylates was adopted as a tentative method.

(d) The bromine method[3] for the determination of total salicylates was adopted as a tentative method.

(e) The double titration method[4] for the determination of acetylsalicylic acid was adopted as a tentative method.

(2) Under the heading, "Camphor", methods[5] for the determination of monobromated camphor were adopted as tentative methods.

(3) Under the heading, "Alkaloids", a method[6] for the separation of quinine and strychnine was adopted as a tentative method.

(4) Under the heading, "Physostigma", a method[7] for the assay of the drug and its preparations was adopted as a tentative method.

(5) Under the heading, "Hyoscyamus" a method[8] for the assay of the extract of hyoscyamus and its preparations was adopted as a tentative method.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 292.
[2] *Ibid.*, 514.
[3] *Ibid.*, 582.
[4] *Ibid.*, 583.
[5] *Ibid.*, 587.
[6] *Ibid.*, 1921, 4: 416.
[7] *Ibid.*, 418.
[8] *Ibid.*, 1922, 5: 569.

(6) Under the heading, "Strychnine", the following methods were adopted:

(a) A method[1] for the assay of strychnine in tablets, including the volumetric procedure, as an official method. (First action as an official method.)

(b) A method[2] for the assay of strychnine in liquids, including the volumetric procedure, as an official method. (First action as an official method.)

(7) Under the heading, "Morphine, Codeine and Diacetylmorphine", methods[3] for the qualitative test and the quantitative determination of morphine, codeine and diacetylmorphine were adopted as tentative methods.

(8) Under the heading, "Arsenicals", the following additions were made to the methods:

(a) Qualitative tests[4] for the identification of arsphenamine and neoarsphenamine were adopted as tentative methods.

(b) A method[5] for the determination of arsenic in arsphenamine and neoarsphenamine was adopted as a tentative method.

XXIX. SOILS.

No additions or changes were made at the 1921 meeting.

XXX. REFERENCE TABLES.

No additions or changes were made at the 1921 meeting.

Respectfully submitted,

R. E. DOOLITTLE, J. W. SALE,
B. B. ROSS, G. W. HOOVER,
A. J. PATTEN, W. H. MACINTIRE.

Committee on Editing Methods of Analysis.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 564.
[2] *Ibid.*, 566.
[3] *Ibid.*, 150.
[4] *Ibid.*, 526.
[5] *Ibid.*, 527.

Later, after extended discussion as to policy, expense likely to be incurred and form of publication, it was moved that the Association approve the plan of the American Public Health Association for a joint publication of the bacteriological and chemical methods for the examination of milk on condition that the identity of the chemical methods as the A. O. A. C. methods be retained in such a publication and that the Board of Editors be authorized to attend to the details of such a publication.

The motion was seconded and carried.

REPORT OF THE BOARD OF EDITORS.

By R. W. Balcom (Bureau of Chemistry, Washington, D. C.), *Chairman.*

Not long after the convention last year the association lost the services of Miss Nellie A. Parkinson, who resigned her position in the Bureau of Chemistry to become assistant to the editor of the *Journal of Industrial and Engineering Chemistry.* For some time Miss Parkinson had acted as associate editor of *The Journal* and upon her as such had devolved the work of editing and preparing for publication the material published therein. This work is now being very ably done by Miss Marian E. Lapp

No. 3 of Volume V of *The Journal,* or the February, 1922 issue, carried the last of the proceedings of the 1920 meeting and the first of the proceedings of the 1921 meeting. No. 2 of Volume VI, which is the November, 1922 number, is about ready for mailing and, in additionto the final part of the proceedings of last year's convention, will contain a few contributed articles. Thus, for the first time in the history of *The Journal,* it will be possible to begin the editing of current proceedings just as soon as the convention closes. The irregularity in the dates of issuance during the past year has been due to no fault of the editorial office, but to indifferent service on the part of the printer. The material for the August number, for example, was in the hands of the printer before the end of June, but that number was not ready for mailing until a few days ago, some four months later. It was recognized some time ago that this condition of affairs could not be allowed to continue, and negotiations with other printers were begun. These have not as yet been concluded, but there is every prospect that better service and a material reduction in charges for printing will soon be obtained, either from the company now doing the work or from another.

The present list shows 856 subscriptions to *The Journal.* Of these 745, including 34 Canadian, are domestic. This is a decrease of 37 in the domestic subscriptions reported last year, but the Canadians are not responsible for the decrease, as they have increased their subscriptions by four. The foreign subscriptions have increased from 86 to 111, distributed as follows: Africa, 2; Argentina, 2; Australia, 20; Brazil, 2; Chile, 1; China, 2; Czechoslovakia, 1; Denmark, 2; Egypt, 3; England, 21; France, 2; Germany, 1; Holland, 4; India, 28; Ireland, 3; Italy, 1; Japan, 6; Mexico, 1; Norway, 2; Scotland, 5; West Indies, 2. Doubtless the decrease in domestic subscriptions is to be attributed largely to the business depression from which the country now seems to be emerging. Chemists and the chemical industries have been particularly hard hit by this depression. Many individuals have been forced to economize in every possible way. The members of this association, however, have probably suffered less than the chemists in industrial

laboratories, and the Board of Editors must again direct your attention to the imperative necessity for increased support of *The Journal* on the part of the individual members of the association. Personal subscriptions from individual members of the association constitute, at the present time, less than 15 per cent of the total number of subscriptions to *The Journal.* Each member should constitute himself a committee of one for the solicitation of subscriptions, including perhaps his own, and bear in mind that *The Journal* now offers a medium of publication for any good papers, particularly of an analytical character, of general or special interest to agricultural chemists.

While the inability to report an increase of subscriptions to *The Journal* is disappointing, there is some consolation in the fact that more than 600 copies of the *Book of Methods* have been sold during the past year. It was reported last year that 1000 additional copies were being printed, but 1224 copies were actually run off by the printer, so that we still have some 600 copies of the *Book of Methods* with which to meet the demand for the coming year. These are all bound and entirely paid for.

As an offset to this, the board has to report that shortly after the meeting of the association last year, Messrs. Frank, of Frank, Emory and Beeuwkes of Baltimore, and Sherier of Leckie, Cox and Sherier of Washington, presented a bill for $500 for legal services rendered in connection with the suit brought by the Williams & Wilkins Company, former publishers of *The Journal.* The Executive Committee, to whom the association had delegated power to act in the matter, decided, and it is thought wisely, to authorize the payment of this bill and close this unfortunate episode in *The Journal's* history. The bill has been paid, as stated in the Secretary-Treasurer's report, in part with funds from dues and in part from funds credited to *The Journal's* account.

Another matter that should be recorded is the closing out of the so-called guaranty fund established during the years 1914 and 1915. Its purpose, inferred from its name, was to create a fund from which, in case of necessity, the association could draw to make up any deficit incurred in financing *The Journal.* The amounts pledged and actually paid into this fund were not sufficient to increase materially the association's assets. The $127.80 paid in was deposited in a savings bank and carried as a separate account. The Executive Committee, at the 1921 convention, authorized the return of this money on a pro rata basis to the original contributors. The chairman of the Board of Editors, then serving also as the secretary of the association, transferred this fund, which with accrued interest amounted to $148.54, to *The Journal* account and checked it out to the original contributors or their heirs or, as was done in two instances at the contributor's request, credited their share toward current subscriptions to *The Journal.* This disposition of the

guaranty fund seemed to be both expedient and just since this money was not donated outright to the association and necessitated the carrying of an additional account. It was also believed that this evidence of appreciation on the part of the association of the conditions under which the money was contributed would be of equal or greater value to the association at this time than the fund itself.

A financial statement covering receipts and disbursements in connection with the association's two publications, *The Journal* and *The Book of Methods*, is appended as a part of this report. This does not show the amount of the unpaid bills. The bill of July 27 for the printing of No. 4 of Volume V is still unpaid and that of May 31 for No. 3 of Volume V is paid only in part. The bill for No. 1 of Volume VI has not as yet been rendered. It has not been possible to get out of debt during the past year, but the new association year will begin without some of the difficulties and complications that were confronted a year ago. The Board of Editors is doing its utmost to reduce expenses and at the same time maintain, or even improve, the quality and usefulness of *The Journal*, but it must have the active, earnest support of every member of the association. It is handicapped by the deficit, which could not be decreased during the past year, and it will be restricted in independence of action until that deficit has been wiped out. The board will welcome and appreciate any suggestions either now or in writing at any other time.

This report can not be closed without a word of appreciation of the services of Dr. William Frear, of Pennsylvania. Dr. Frear took a most active part in the deliberations of the association which led to the establishment of *The Journal* and served as a member of the Board of Editors until he died. The news of his sudden death in January came as a profound shock to the other members of the board. A fitting tribute to Frear as a scientist and as a man, prepared by one of the members of the association, was printed in the May issue.

Approved.

FINANCIAL REPORT ON PUBLICATIONS FROM

By R. W. Balcom (Bureau of Chemistry,

RECEIPTS.

1921					
Oct. 15	Bank balance			$	162.63
	Total deposits		$ 7,686.22		
	Less redeposited checks	$ 24.00			
	Less exchange on check for $5.00	.10			
			24.10		
					7,662.12
					$7,824.75

DETAILED STATEMENTS RELATIVE TO RECEIPTS.

Journal Subscriptions.

No. Ordered	Price Each	Total Cost
56	$5.50	$ 308.00
457	5.00	2,285.00
73	4.40	321.20
221	4.00	884.00
70	3.75	262.50
35	3 00	105.00
9	2.50	22.50
6	1.75	10.50
18	1.50	27.00
4	1.40	5.60
15	1.25	18.75

Total	$ 4,250.05	
Plus gain through exchange	1.40	
Total		$ 4,251.45

OCTOBER 16, 1921 TO NOVEMBER 1, 1922.

Washington, D. C.), *Chairman, Board of Editors.*

DISBURSEMENTS.

Date		Amount	Check No.*
1921			
Nov. 2	N. A. Parkinson, office expenses	$ 25.00	117
Nov 5	C. L. Alsberg, refund on Guaranty Fund	1.16	118
Nov. 5	Edmund Burke, refund on Guaranty Fund	5.81	119
Nov. 5	Mrs. W. C. Burnett, refund on Guaranty Fund	5.82	120
Nov. 5	G. W. Hoover, refund on Guaranty Fund	27.90	121
Nov. 5	W. M. Cobleigh, refund on Guaranty Fund	5.82	122
Nov. 5	R. E. Rose, refund on Guaranty Fund	5.82	123
Nov. 5	G. S. Fraps, refund on Guaranty Fund	11.62	124
Nov. 5	H. C. Gore, refund on Guaranty Fund	5.81	125
Nov. 5	Herman Harms, refund on Guaranty Fund	5.58	126
Nov. 5	E. H. Jenkins, refund on Guaranty Fund	5.81	127
Nov. 5	C. H. Jones, refund on Guaranty Fund	11.62	128
Nov. 5	H. M. Loomis, refund on Guaranty Fund	11.63	129
Nov. 5	P. S. Tilson, refund on Guaranty Fund	5.81	130
Nov. 5	A. S. Wells, refund on Guaranty Fund	5.81	131
Nov. 5	H. E. Wiedemann, refund on Guaranty Fund	5.81	132
Nov. 7	A. T. Charron, refund on subscription	3.00	133
Nov. 7	City Treasurer, Dallas Tex., refund on subscription	1 00	134
Nov. 8	R. W. Hilts, refund on subscription	6.00	135
Nov. 8	R. S. Hollingshead, refund on subscription	1.00	136
Nov. 8	Industrial Printing Co., 1000 stickers for *Book of Methods*	9.75	137
Nov. 14	Fritzsche Bros., refund on subscription	1.25	138
Nov. 15	Louise Calouge, refund on subscription	2.50	139
Nov. 16	Schwarz Laboratories, refund on subscription	1.25	140
Nov. 16	C. Milan Morse, refund on subscription	1.25	141
Nov. 17	Industrial Chemical Institute of Milwaukee, refund on subscription	1.25	142
Nov. 19	Charles H. LaWall, refund on subscription	1.25	143
Nov. 19	H. H. Hanson, refund on subscription	2.00	144
Nov. 19	H. Kohnstamm & Co., refund on subscription	1.25	145
Nov. 19	N. A. Parkinson, office expenses	25.00	146
Dec. 10	Moore-Cottrell Subscription Agencies, refund on subscription	1.00	147
Dec. 10	Crescent Manufacturing Co., refund on subscription	1.25	148
Dec. 10	George A. Olson, refund on subscription	1.25	149
Dec. 10	Ware Brothers, refund on subscription	1.25	150
Dec. 13	Fred W. Nestelle, refund on subscription	1.25	151
Dec. 13	Francis H. Leggett, refund on subscription	1.25	152
Dec. 15	Cash, office expenses	10.00	153
Dec. 15	Industrial Printing Co., on account	1,000.00	154
1922			
Jan. 4	R. W. Balcom, reimbursement for freight charges on *Journal*	3.78	155
Jan. 5	Brentano's, refund on subscription	.50	156
Jan. 6	Cash, office expenses	25.00	157
Jan. 6	Postmaster, box rent for quarter ending Mar. 31	2.00	158
Jan. 6	National Biscuit Co., refund on subscription	1.25	159
Jan. 7	State of Minnesota, refund on subscription	12.00	160
Jan. 12	C. A. Browne, refund on subscription	1.25	161
Jan. 14	E. H. Berry, refund on subscription	2.00	163
Jan. 16	R. S. Thompson, refund on subscription	1.25	164
Jan. 21	Industrial Printing Co., on account	643.85	165
Feb. 1	C. H. Jones, refund on subscription	2.00	166
Feb. 7	W. J. Jones, refund on Guaranty Fund	5.81	167
Feb. 7	J. W. Watson, refund on Guaranty Fund	1.16	168
Feb. 7	Mrs. A. M. Davidson, refund on Guaranty Fund	1.16	169
Feb. 7	Mississippi A. and M. College, refund on Guaranty Fund	5.81	170
Feb. 9	University of Tennessee, refund on Guaranty Fund	1.16	171

RECEIPTS—*Continued.*

Methods Subscriptions.

No. Ordered	Price Each	Total Cost		
35	$5.50	$ 192.50		
445	5.00	2,225.00		
44	4.40	193.60		
145	4.00	580.00		
Total		$ 3,191.10		
Plus gain through exchange		1.60		
Total			$ 3,192.70	
Total, Journal and Methods				$ 7,444.15
Excess payments			71.75	
Plus bank balance			162.63	
Guaranty Fund less $2.32*			146.22	
				380.60
				$7,824.75

*Credited at contributor's request toward payment on subscription to Journal.

DISBURSEMENTS—*Continued.*

1922		Amount	Check No.*
Feb. 18	Robert Stewart, refund on Guaranty Fund	1.16	172
Feb. 27	Industrial Printing Co., on account	500.00	173
Feb. 28	George P. Gray, refund on Guaranty Fund	1.16	174
Feb. 28	Lucy S. Patrick, refund on Guaranty Fund	5.81	175
Feb. 28	E. J. Lea, refund on Guaranty Fund	1.16	176
Feb. 28	Janet K. Smith, office expenses	25.00	177
Mar. 17	Janet K. Smith, office expenses	25.00	178
Mar. 18	Industrial Printing Co., on account	500.00	179
Mar. 23	Armour and Co., reimbursement on duplicate payment on order No. 107610	5.00	180
Mar. 24	Franklin Institute, refund on subscription	1.25	181
Mar. 29	American News Co., reimbursement on duplicate payment on order No. G-506	4.00	182
Mar. 30	Postmaster, box rent for quarter ending June 30	2.00	183
Apr. 7	Tennessee Coal, Iron and Rail Road Co., reimbursement on order No. 78099	5.00	184
Apr. 20	Janet K. Smith, office expenses	25.00	185
Apr. 21	Industrial Printing Co., on account	619.86	186
May 10	R. W. Balcom, reimbursement on trip to Baltimore	2.50	187
May 12	Industrial Printing Co., on account	500.00	188
May 16	Leckie, Cox and Sherier, lawyers' fees	250.00	189
June 2	Janet K. Smith, office expenses	10.00	190
June 2	Industrial Printing Co., on account	584.09	191
June 8	Farran's Transfer and Storage, delivering *Journals*	3.71	192
June 8	Janet K. Smith, office expenses	25.00	193
July 1	Postmaster, box rent for quarter ending Sept. 30	2.00	194
July 8	Williams & Wilkins, back numbers of *Journal*	5.45	195
July 17	Industrial Printing Co., on account	500.00	196
July 27	Williams & Wilkins, back number of *Journal*	1.25	197
Aug. 1	R. E. Rose, refund on subscription	1.00	198
Aug. 7	Williams and Wilkins, back number of *Journal*	1.25	199
Aug. 7	Farran's Transfer and Storage, delivering *Journals*	4.11	200
Aug. 10	Louis A. Voorhees, refund on subscription	1.00	201
Aug. 11	H. H. Hanson, refund on subscription	1.00	202
Aug. 12	Janet K. Smith, office expenses	30.00	203
Aug. 14	Industrial Printing Co., on account	500.00	204
Aug. 14	Ontario Agricultural College, refund on subscription	1.00	205
Sept. 8	Industrial Printing Co., on account	400.00	206
Sept. 22	Postmaster, box rent for quarter ending Dec. 31	2.00	208
Sept. 22	Industrial Printing Co., on account	218.65	209
Sept. 22	Janet K. Smith, office expenses	25.00	210
Oct. 3	R. W. Hilts, refund on subscription	1.00	211
Oct. 10	Industrial Printing Co., on account	342.95	212
Oct. 19	Paul Elder & Co., refund on *Book of Methods*	1.00	213
Oct. 19	Industrial Printing Co., on account	400.00	214
Oct. 30	Cash, office expenses	25.00	215
Oct. 30	Bank balance	332.58	
		$7,824.75	

*Checks 162 and 207 cancelled.

FINANCIAL REPORT OF THE SECRETARY-TREASURER

By W. W. Skinner (Bureau of Chemistry,

RECEIPTS.

1921			
Oct. 16	Bank balance		$ 299.15
1922			
Mar. 18	Dues from 6 Canadian and State institutions received too late for inclusion in 1921 report	$ 30.00	
	Dues for 1922 from 37 Canadian and State institutions*	185.00	
			215.00
Aug. 8	Dues from 2 State institutions received too late for inclusion in 1921 report	$ 10.00	
	Dues for 1922 from 9 State institutions	45.00	
			55.00
Oct. 31	Dues for 1922 from 9 Canadian and State institutions		45.00
	Total receipts		$ 614.15

*Check for $5.00 from University of California for *Journal* deposited in Secretary-Treasurer account in error.

FROM OCTOBER 16, 1921 TO NOVEMBER 1, 1922.

Washington, D. C.).

DISBURSEMENTS.

		Amount	Check No.
1921			
Nov. 23	N. A. Parkinson, reimbursement for expenses, 1921 meeting.	$ 51.60	18
1922			
Mar. 17	Cash, cost of telegram sent to State College by F. P. Veitch	.91	19
May. 16	Leckie, Cox and Sherier, lawyers' fees	250.00	20
Aug. 16	R. W. Balcom, check for $5.00 from University of California deposited to Secretary-Treasurer account in error. Check given Dr. Balcom to be credited to *Journal* account	5.00	21
Sept. 25	Janet K. Smith, cash for postage for mailing announcements of meeting	20.00	22
Oct. 4	Byron S. Adams, 1500 programs, 1922 meeting	41.75	23
Oct. 25	Bastian Bros., badges, 1922 meeting	28.02	24
Oct. 31	Bank balance	216.87	
	Total	$ 614.15	

Approved.

President Veitch: I should like to speak again of what the Chairman of the Board of Editors referred to. The success of *The Journal* is an important matter to us and to this association. In the report this morning it was brought out that somewhere between 10 and 15 per cent—nearer 10 per cent—only of the subscriptions are from individual members of the association. Now, *The Journal* can not go on in that way without increasing the deficit rather than decreasing it and I am sure you will all be interested to know this and to help all you can.

R. E. Doolittle: I wonder if, as a member of the Board of Editors, I might add a word in that connection. The Board of Editors met and we spent half a day in discussing this matter. The matter is really serious. The Board of Editors—Dr. Balcom principally—has laid out plans for the coming year to reduce expenses just as much as possible. We hope to accomplish something in that way and also by increasing the number of subscribers. The appeal has been made by Dr. Balcom and by your president but I want to tell you now that if we come here next year with no better financial condition than we are showing this year, some radical change will have to be made. We want the earnest support of every member of this association if we are going to succeed.

President Veitch: A world's dairy congress is to be held in October, 1923. Mr. Van Norman, President of the World's Dairy Congress Association, will tell us very briefly something about this coming congress, because chemists are interested in dairy matters.

H. E. Van Norman: The plans are to hold this congress next October near whatever city is chosen as the site for the National Dairy Show of that year. I do not know just which city it will be. We had some hopes of Philadelphia. The thought is to develop a program for the discussion of the things relating to the dairy cow and her products, the program to be so arranged as to interest four groups of people: first, those who view these problems from the scientific and educational standpoint, such as college men, research men, etc.; second, those who view them from a business standpoint, all the way from the farmer, manufacturer, distributor, equipment man, etc.; third, those who view them as law enforcement officials with all the things relating thereto; and fourth, those who are interested in these problems only from the standpoint of their relation to public welfare.

It is our hope to bring to this country some of the leading men interested in these aspects of the problem internationally. I invite those of you who are interested in these subjects as chemists to cooperate with us in making this a worth-while program. Perhaps you would like to appoint a committee which would be interested in these aspects of the meeting to cooperate in our program work.

A motion was made, seconded and carried that a committee of three members be appointed by the president to collaborate in formulating the program of the World's Dairy Congress.

Later A. J. Patten, the newly elected president of the association, appointed the following to serve on this committee: E. M. Bailey, New Haven, Conn., Chairman; E. L. Van Slyke, Geneva, N. Y.; and H. W. Redfield, New York, N. Y.

No report was made by the Committee on Quartz Plate Standardization and Normal Weight.

President Veitch: If there is any work which requires more courage than being a farmer, it is that of being the Secretary of Agriculture. It has been my privilege to work under four successive Secretaries of Agriculture, all of whom have contributed something of value to agriculture and to the work of the Department. They have always extended their encouragement to this association and to its members, and not one has been more active and successful in this particular than has the present Secretary of Agriculture, Secretary Wallace, whom it is now my great pleasure to introduce to you.

ADDRESS BY THE SECRETARY OF AGRICULTURE—THE HONORABLE HENRY C. WALLACE.

I am glad of an opportunity to come to you once a year and make due acknowledgment of the fine service we have received from you. Our Departmental work would go along much more slowly and much less efficiently but for your fine cooperation. I am under personal obligations to you in the benefit I am getting from the committee which you appoint on standards. It gives me, very frequently, the opportunity to "pass the buck" to your strong hands. I want to express my appreciation in this public way to the members of the committee as well as to the members of the association from which the committee springs.

We are your beneficiaries in the manner in which you work out standards of analysis—beneficiaries in two ways: First, those methods are helpful to us in our administration of certain of the regulatory laws with which we are charged; and second, they are helpful to the entire cause of agriculture in that they are necessarily fundamental and help to establish methods which can be used not alone by you in your official capacity but by scientists in that field everywhere. I believe that the developments of the past two years emphasize more than ever before the importance of that sort of work.

If you will permit me, Mr. Chairman, I want to speak just a moment of the general conditions in agriculture at this time and how I think the

chemists are going to tie into the work that is being done to help bring about improved conditions. I just completed my annual report yesterday. I completed it yesterday because it had to be completed yesterday by law. I have wondered sometimes, if it were not due on an exact day, how long it would take to get out an annual report. As compared with a year and a year and a half ago, farm prices have advanced very considerably. In some cases, especially in the case of cotton, the advance has been very substantial; but when we size up the whole matter from the economic side as the farmer is affected we find this—that whereas farm prices have advanced, prices of other things have advanced in just about the same proportion. So, if we compare the farmer's buying capacity, his purchasing power—that is, what he can get for what he grows—with his situation a year ago, we find that with the exception of the cotton region, there has not been that improvement that we had hoped there might be. We have been studying that situation in the Department with a great deal of intensity, because we feel under obligation to help make a prosperous as well as a productive agriculture. You can not have a continuing productivity in agriculture unless it is also prosperous. Thus, our study has developed a movement in which I think you may be interested.

We are setting up commodity councils. We are bringing in once or twice a week, for example, every one in a position of large responsibility in the Department who touches cotton in any way in the effort to work out a definite Departmental policy as regards cotton so that we will be able to give to our extension people certain definite Departmental policies. We bring in the soil people, who display their maps showing the different kinds of soils and how cotton growth is influenced by soil. We bring in the varieties people, the cultural people, and the entomologists whose work deals with the boll weevil and other insect pests. Now, after we have worked these matters out to our own satisfaction within the Department, we are expecting to have conferences in the regions interested in cotton, that is with the agricultural college people and the State boards of agriculture where that particular crop is grown. They will check up on our policy by making suggestions or modifications and contributing whatever views they have to contribute. From our Departmental program, after it is formed, we will have a definite program to carry out through the various extension agents. I think that this development will lead to the consideration of the entire agriculture of the region also, that is the effects of changes in cotton on other crops. We are starting another commodity council in the Northwest based on wheat primarily, because that is the one big crop.

It is evident from the economic developments growing out of the war, both over seas and at home, that the changes in freight rates are going to have a profound influence on both our agriculture and industry. It

is also evident that there must be much more definite and concrete policies affecting the agriculture of various crops and of various regions. When we get into that phase of the subject, if it works as we think it will, the chemist will have an increasingly important part. The question of the best utilization of the crops grown in a particular section and the question of the utilization of other crops which may be grown to meet the needs of the section will be important.

I was greatly interested the other day in a report brought to me by a man from Arizona. He, as secretary, came to ask me down to their industrial conference. He said: "We found many of our industries, as well as our agriculture, in bad shape during the past two years and we called a meeting asking delegates from all the various industries. That meeting was composed of three delegates from each of the major industries of the State. Our packing industry was in bad shape. We set up a movement to promote the consumption of meat from our own packing houses within the State. The packers now are in a fairly prosperous condition. Then the lumber people said that their mills were shut down as they had no work to do. Our manager went to the railroad people first and got an order from them for four million ties; through that order our lumber mills started up again. Now most of our industries are in good shape. In other words, the people of Arizona are considering the interests of Arizona as well as of all the industries in it and meshing them into one another. In the case of potatoes, our potato growers were marketing them without regard to the interests of one another. We organized them into commodity councils. The potatoes from one section are now marketed at one time and those from another section at another time". What is the result? It is just an attempt to put the agriculture of the country on a sound basis. The chemists will have to mesh into the work in innumerable ways, and as time goes on and as modifications which must come, do come, the chemist's office in the work will assume increasing importance.

So I am glad to have an opportunity to come and pay my respects to you, to lay a larger responsibility on you, and to wish you all possible success in your meeting here.

President Veitch: I should like to call attention to the fact that we have three amendments to the by-laws to be voted upon. These amendments were also read on Wednesday.

The first amendment is as follows:

A Board of Editors of *The Journal* of the association, consisting of five members, one of whom shall be designated the chairman, shall be appointed by the president upon recommendation of the Executive Committee. These five members shall serve one, two, three, four and five years, respectively, and each following appointment shall be for five years.

The motion to adopt this amendment to the by-laws was seconded and carried.

President Veitch: The two following amendments were presented by the Committee on Definitions of Terms and Interpretation of Results on Fertilizers:

(1) A fertilizer definition or interpretation shall not be adopted as tentative or a tentative definition or interpretation amended until such definition or interpretation has been recommended by the Committee on Definitions of Terms and Interpretation of Results on Fertilizers and published in the proceedings of the association.

(2) A fertilizer definition or interpretation shall not be adopted as official or an official definition or interpretation be amended until such definition or interpretation has been recommended by the Committee on Definitions of Terms and Interpretation of Results on Fertilizers for at least two annual meetings.

The motion to adopt these two amendments to the by-laws was seconded and carried.

REPORT OF COMMITTEE ON VEGETATION TESTS ON THE AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG.

Results of the cooperative vegetation pot and field experiments, made under the direction of your committee, have been assembled in abbreviated form, in accordance with a vote of the association taken in 1921. The committee has been over the work and some changes have been made with reference to the form of presenting the final summaries. This will necessitate revising the manuscript before it passes into the hands of the publishers of *The Journal.* This work can likely be accomplished, however, so that it will not delay publication of the report. It would not seem necessary to continue the services of the committee after the manuscript is in final form for publication, and it is hoped that the association may so vote. Your committee would make the following formal report at this time:

The Basic Slag Committee, after carefully reviewing the work of the different collaborators, as incorporated in the final report which has been prepared for publication in the association's journal, wishes to recommend that the Wagner method for the determination of the available phosphoric acid in high-grade basic slag phosphate be adopted by the association as official. (Second reading.)

H. D. HASKINS, B. L. HARTWELL,
J. A. BIZZELL, C. B. WILLIAMS.
W. B. ELLETT,

Committee on Vegetation Tests on the Availability of Phosphoric Acid in Basic Slag.

Approved.

After the formal report was presented, by vote of the association the committee was discharged. The association voiced an expression of thanks for the services of the committee.

REPORT OF COMMITTEE TO COOPERATE WITH THE AMERICAN SOCIETY FOR TESTING MATERIALS IN REGARD TO METHODS OF ANALYSIS FOR LIMING MATERIALS.

The committee held several meetings and conferences with two sub-committees of Committee C-7, Sub-Committee for Agricultural Lime and Sub-Committee for Methods of Analysis of Liming Materials, of the A. S. T. M. Two members of the committee also held a conference with officials of the Bureau of Standards who have collaborated with the A. S. T. M. in the preparation of tentative methods. It was agreed that uniformity in the methods of the two bodies would prove desirable. It was further agreed, however, that precision requirements are not identical for liming materials for industry and agriculture.

Your committee desires to stress the fact that liming materials have received no recognition by promulgation of methods for their control though a number of States have in operation regulatory lime laws in parallel to those for fertilizer control. The already extensive and rapidly expanding usage of lime materials necessitates the adoption of official methods for the sampling and analysis of the several commercial lime products.

Your committee does not feel sure that it was empowered to compile a chapter of methods on the analysis of liming materials. It is unanimous, however, in the belief that there exists an imperative need for such a chapter. Most of the determinations necessary to such a compilation are already official as related to other materials. Your committee, therefore, recommends that it, or a superseding personnel, be directed to compile a chapter on "Liming Materials", adapting present official procedures to the analysis of liming materials, and that such additional methods as may be necessary be subject to collaborative study with a view to tentative or official adoption.

Respectfully submitted,

W. H. MacIntire,
F. P. Veitch,
J. B. Weems.

Approved.

No report was made by the Committee on Revision of Methods of Soil Analysis.

REPORT OF COMMITTEE ON RECOMMENDATIONS OF REFEREES.

By R. E. DOOLITTLE (Food and Drug Inspection Station, Chicago, Ill.), *Chairman.*

You have heard the reports of the chairmen of Subcommittees A, B and C which represent the real work of your Committee on Recommendations of Referees. Due consideration has been given to all referee reports submitted and each and every recommendation has been carefully examined not only in connection with the analytical data and other information submitted in the reports of this year but also with that of former years in order that the high standard of excellence which the methods of the association enjoy in the scientific and industrial fields shall be upheld.

Your committee desires to congratulate the referees and associate referees on the splendid reports which have been submitted this year. To single out an individual report would be unfair, but your committee can not pass the opportunity to call attention to the number of collaborators and the completeness of their analytical results as reported by the referee on crude fiber. To your committee this illustrates the interest and enthusiasm the members of the association have in methods of primary importance in agricultural and analytical chemical work.

Your committee has noted from reports submitted that there appears to be some confusion or misunderstanding as to the form of action to be recommended for making a method tentative or official. In this connection the attention of the referees is called to the following sections of the by-laws of the association.

(5) A method shall not be adopted as official or an official method be amended until such method or amendment has been recommended for at least two annual meetings by the appropriate referee.

(7) A method shall not be adopted as tentative or a tentative method amended until such method or amendment has been reported by the appropriate referee and published in the proceedings of the association.

Taking the two classes of methods in the inverse order, it is to be noted that the requirements for a tentative method are two: First, that it shall be recommended by the appropriate referee; and second, that it shall have been published in the proceedings of the association. Your committee notes an occasional recommendation that a method be adopted as a tentative method, second action. Such a recommendation is incorrect. A method once adopted as a tentative method remains tentative until changed, deleted or made official. If, as the result of study of a tentative method, a referee concludes that the method should remain tentative, a recommendation that it be continued as a tentative

method should be made, not that it be a tentative method, second action. If, as a result of his study, he desires to change a tentative method, he should recommend that the changed or modified method be adopted as a tentative method. In other words, a method may be adopted as a tentative method by one action of the association, or a change may be made in a tentative method by one action of the association. This is one of the points of distinction between an official and a tentative method. A method can be made official only when so recommended by the appropriate referee for at least two annual meetings of the association. Your committee interprets this provision of the by-laws to mean that to become official a method must be recommended for adoption as an *official method* at at least two annual meetings. The adoption of a method as a tentative method at one meeting does not entitle it to be adopted as a final official method at the next meeting or, in other words, a method must be recommended for adoption as official by two referees or by the same referee at two different meetings. A method may be adopted as a tentative method and as an official method, first action, at the same meeting. When this is desired, a definite recommendation to that effect should be made in the referee's report. Section 2 of the by-laws of the association provides:

> These by-laws or any portion of them may be suspended at any regular meeting of the association without previous notice by a vote of three-fourths of the active members present.

Under this by-law, the provisions above referred to may, by a three-fourths vote of the active members present, be suspended and a method adopted as a tentative method or as an official method immediately. This apparently is intended to take care of emergencies that may arise from time to time. When such an action is desired a definite recommendation to that effect with the reasons therefor should be incorporated in the referee's report.

These forms of procedure are referred to for the information of the referees and associate referees in order that their recommendations may be uniform, thus expediting the work of the Committee on Recommendations of Referees in the consideration of reports, the time for which is necessarily limited.

In accordance with the provisions of Article III of the constitution of the association, your committee has prepared a list of referees and associate referees for the coming year, which list will be announced by the president.

Approved.

REPORT OF COMMITTEE A ON RECOMMENDATIONS OF REFEREES.

By B. B. Ross (Alabama Polytechnic Institute, Auburn, Ala.), *Chairman.*

[Fertilizers (boric acid in fertilizers, preparation of ammonium citrate, nitrogen, potash, potash availability, precipitated phosphates, vegetation tests on availability of phosphoric acid in basic slag), inorganic plant constituents (calcium, magnesium, iron and aluminium in the ash of seed; sulfur and phosphorus in the seeds of plants), water, tanning materials and leather, insecticides and fungicides, and soils (sulfur in soils).]

FERTILIZERS.

BORIC ACID IN FERTILIZERS.

It is recommended—

(1) That as boron compounds not soluble in water but soluble in weak acids appear to be as injurious to plants as the water-soluble compounds and since the Bartlett distillation method[1] as now carried out determines the boron in such compounds, it be adopted as an official method in its present form to determine boron in mixed fertilizers and fertilizer materials. (First action as an official method.)

Approved.

(2) That a further study be made of the modification of the Ross-Deemer method outlined in the second recommendation of the referee with a view to determining its adaptability to the estimation of boron in boron compounds insoluble in water, but soluble in weak acids.

Approved.

(3) That the Ross-Deemer method as given by the referee for 1921[2] be adopted as an official method to determine water soluble boron in mixed fertilizers and fertilizer materials. (First action as an official method.)

Approved.

PREPARATION OF AMMONIUM CITRATE.

The committee recommends the approval of the recommendation of the associate referee that the method for the preparation of ammonium citrate solution[3] be adopted as official, but does not recommend the deletion, at this time, of the present official method. (First action as an official method.)

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1921, **5**: 90.
[2] *Ibid.*, 1922, **5**: 327.
[3] *Ibid.*, 445.

NITROGEN.

It is recommended—

(1) That the referee for 1923 be instructed to study the Devarda method[1] as applied to the nitrates of commerce.

Approved.

(2) That the Moore method[2] for nitrates be studied with collaborators next year.

Approved.

(3) That the referee on nitrogen for 1923 be instructed to study the use of sodium thiosulfate as a substitute for sodium or potassium sulfide in precipitating mercury in the Kjeldahl method.

Approved.

POTASH.

It is recommended—

(1) That the investigation of the centrifugal method by Sherrill be discontinued.

Approved.

(2) That the general referee on fertilizers for the ensuing year study the literature with regard to the use of alcohol stronger than 80 per cent for washing the potash precipitate with a view to ascertaining if collaborative investigation of the question is desirable.

Approved.

POTASH AVAILABILITY.

No report or recommendations.

PRECIPITATED PHOSPHATES.

It is recommended—

That the determination of insoluble phosphoric acid in precipitated phosphates be carried out according to the present official method for the determination of insoluble phosphoric acid in fertilizers[3], with the exception that a 1-gram charge be employed. (Second action as an official method.)

Adopted.

VEGETATION TESTS ON AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG.

The committee recommends the final adoption of the following recommendation of the Committee on Vegetation Tests presented at the meeting in 1921:

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 451.
[2] *J. Ind. Eng. Chem.*, 1920, **12**: 669.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 4.

It is the opinion of your committee that the tentative Wagner method[1] is a reliable procedure for measuring the available phosphoric acid in basic slag phosphates and it would, therefore, recommend that it be adopted by the association as official. (Second action as an official method.)

Adopted.

INORGANIC PLANT CONSTITUENTS.

CALCIUM, MAGNESIUM, IRON AND ALUMINIUM IN THE ASH OF SEED.

It is recommended—

(1) That the incoming referee make a study of the entire chapter, (II)[2], before another general revision is made, with a view to deleting any unnecessary methods.

Approved.

(2) That the methods for iron, aluminium, calcium and magnesium, as given in the referee's report, be further studied with a view to their adoption as tentative methods.

Approved.

SULFUR AND PHOSPHORUS IN THE SEEDS OF PLANTS.

It is recommended—

(1) That the magnesium nitrate method for the determination of sulfur in plant material including the seed of plants, as outlined in the report of the associate referee, be adopted as a tentative method.

Approved.

(2) That the determination of phosphorus from the sulfur determination be also adopted as a tentative method.

Approved.

WATER.

It is recommended—

(1) That the following methods be adopted as tentative:

(a) Lead and zinc[3].

Approved.

(b) Copper, as given on page 107.

Approved.

(2) That additional methods for the analysis of salt[4] be studied next year.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 14.
[2] *Ibid.*, 15.
[3] *J. Assoc. Official Agr. Chemists*, 1922, 5: 382.
[4] *Ibid.*, 384.

TANNING MATERIALS AND LEATHER.

It is recommended—

That the work on the determination of tannin in tanning materials be continued.

Approved.

INSECTICIDES AND FUNGICIDES

The committee recommends the adoption of the suggestions of the referee that a study be made of methods of analysis of dusting mixtures.

Approved.

It is further recommended—

(1) That the mercury-thiocyanate method for zinc oxide in zinc arsenite, as given in the referee's report for 1921[1], be adopted as an official method. (Second action as an official method.)

Adopted.

(2) That Method 1 for the determination of calcium oxide in calcium arsenate, as given in the referee's report for 1921[2], be adopted as an official method. (Second action as an official method.)

Adopted.

(3) That Method 2 for the determination of calcium oxide in calcium arsenate, as given in the referee's report for 1921[3], be adopted as an official method. (Second action as an official method.)

Adopted.

(4) That in the "General procedure for the analysis of a product containing arsenic, antimony, lead, copper, zinc, iron, calcium, magnesium, etc.", the method for zinc oxide, as given in the referee's report for 1921[4], be adopted as an official method. (Second action as an official method.)

Adopted.

(5) That the hydrazine distillation method for the determination of total arsenic[5] be adopted as an official method. (First action as an official method; adopted as a tentative method in 1921.)

Approved.

SOILS.

It is recommended—

That further study be made in an effort to secure a mode of procedure which may be used in removing all the sulfates which are carried by a nitric acid soil, or synthetic soil, solution.

Approved.

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 392.
[2] *Ibid.*, 395.
[3] *Ibid.*, 396.
[4] *Ibid.*, 398.
[5] *Ibid.*, 402.

REPORT OF COMMITTEE B ON RECOMMENDATIONS OF REFEREES.

By H. C. LYTHGOE (State Department of Public Health, Boston, Mass.), *Chairman.*

Foods and feeding stuffs (crude fiber, starch, stock feed adulteration), saccharine products (sugar, honey, maple products, maltose products, sugar-house products), dairy products, fats and oils, baking powder, chemical reagents, non-alcoholic beverages, eggs and egg products, drugs.

FOODS AND FEEDING STUFFS.

It is recommended—

(1) That Recommendations 1 and 2 of 1922, relative to sulfur dioxide and chlorine in bleached grain and the acidity of grains other than corn be dropped.

Approved.

(2) That the referee be appointed to study the existing official general methods for water in foods and feeding stuffs with a view to rewording and fixing rigidly the conditions of temperature, pressure and other factors.

Approved.

(3) That a definite method applicable to the determination of water in dried food be designed and submitted to the association.

Approved.

(4) That the work on the comparison of the C. R. Smith[1] and the official[2] methods for the determination of ether extract be continued next year.

Approved.

(5) That further study be made of the effect which grinding the sample finer will have upon the ether extract determinations.

Approved.

CRUDE FIBER.

It is recommended—

That the referee consider the criticisms made of the proposed new method[3] by the collaborators this year and make such studies as may be necessary in order to make a final report relative to the substitution of the proposed method for the official method.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, **6**: 61.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 72.
[3] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 421.

STARCH.

It is recommended—

That a referee be appointed to report upon methods for the determination of starch in linseed meal and similar subjects, as reported in a paper by G. P. Walton.

Approved.

STOCK FEED ADULTERATION.

It is recommended—

(1) That the microscopic method for the determination of rice hulls in rice bran be continued as a tentative method.

Approved.

(2) That the method for the estimation of grit in poultry and similar feeds[1] be adopted as tentative.

Approved.

(3) That the method for the estimation of bone in meat scraps be adopted as tentative[1].

Approved.

(4) That further study be made of microscopic methods for the examination of mixed feeds.

Approved.

SACCHARINE PRODUCTS.

SUGAR.

It is recommended—

(1) That the modifications proposed in 1916 for determining sucrose by acid and invertase inversions be further studied.

Approved.

(2) That the work upon determining small amounts of reducing sugars in the presence of sucrose be continued.

Approved.

HONEY.

It is recommended—

(1) That the work on resorcin and aniline chloride tests[2] for the detection of invertase sugar sirup in honey be further studied in connection with honey heated to a comparatively high temperature. It is suggested that directions to collaborators be more specific as to details of technique and color.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 424.
[2] *J. Assoc. Official Agr. Chemists, Methods*, 1920, 112.

MAPLE PRODUCTS.

It is recommended—

That further study be made of the Canadian lead number and the conductivity value[1].

Approved.

MALTOSE PRODUCTS.

It is recommended—

That the work begun by the referee be continued.

Approved.

SUGAR-HOUSE PRODUCTS.

It is recommended—

(1) That Method III, **12**[2], to determine sulfated ash be discontinued as an official method. (First action in modification of an official method.)

Approved.

(2) That Methods I, **10** and II, **11**[2], relative to ash in molasses, etc., be modified by adding at the end of each method the words: "Take up the residue with a little ammonium carbonate solution, re-evaporate, and heat again in the muffle at a very dull red heat to constant weight".

Approved.

DAIRY PRODUCTS.

It is recommended—

(1) That the cryoscopic method for the examination of milk be adopted as official. (Second action as an official method.)

Adopted.

(2) That the referee on cryoscopic examination of milk be dropped.

Approved.

(3) That the neutral modification of the Roese-Gottlieb method for the determination of fat in malted milk[3] be adopted as tentative.

Approved.

(4) That a further study be made of the Roese-Gottlieb method as applied to dried milk.

Approved.

(5) That a further study be made of the proposed change in the method for fat in unsweetened condensed milk[4] reported upon at the 1921 meeting.

Approved.

(6) That the methods for moisture in cheese reported upon at the

---

[1] *J. Assoc. Official Agr. Chemists*, 1921, **4**: 428.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 105.
[3] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 508.
[4] *Ibid.*, 509.

1921 meeting[1] be subjected to collaborative studies during the coming year.

Approved.

FATS AND OILS.

It is recommended—

(1) That the alternative method for the preparation of the Wijs solution (iodine trichloride method) be not adopted, and further that a statement be inserted in the A. O. A. C. official Wijs method[2] calling attention to the undesirability of using iodine trichloride for the Wijs solution on account of its unstable character.

Approved.

(2) That the sentence beginning "Add 3 cc. of bromine to 200 cc. of acetic acid", **15**, **(a)**[3], be changed to read: "Add 3 cc. of bromine to 200 cc. of acetic acid and titrate 5 cc. of the solution against 0.1N sodium thiosulfate, adding 10 cc. of potassium iodide solution (15 per cent) before titrating". It is recommended that no other change be made in the Hanus method.

Approved.

(3) That the modified Villavecchia test be made official. It is recommended also that the description of the Baudouin and modified Villavecchia tests be changed to read as follows:

SESAME OIL.

Baudouin Test—Official.

Dissolve 0.1 gram of finely powdered sugar in 10 cc. of hydrochloric acid (sp. gr. 1.2), add 10 cc. of the oil to be tested, shake thoroughly for 1 minute and allow to stand for 10 minutes. In the presence of even a very small admixture of sesame oil, the aqueous solution is colored crimson. It should be observed that some olive oils, especially those of African or Spanish origin, give pink or crimson colors which can be readily differentiated from that due to sesame oil by applying the following modification of the Villavecchia method:

Villavecchia Test—Official.

Add 2 cc. of furfural to 100 cc. of 95% alcohol by volume and mix thoroughly 0.1 cc. of this solution with 10 cc. of hydrochloric acid (sp. gr. 1.2), and 10 cc. of the oil to be tested by shaking them together for ¼ of a minute. Allow mixture to stand 10 minutes and observe color. Add 10 cc. of water, shake and again observe color. If the crimson color disappears, sesame oil is not present.

Approved.

(4) That further work be done on the determination of the unsaponifiable matter.

Approved.

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 498.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 245.
[3] *Ibid.*, 244.

(5) That a study be made of the Baudouin and Villavecchia tests using hydrochloric acid of varying specific gravity.

Approved.

BAKING POWDER.

It is recommended—

(1) That Method 2 for the neutralization of monocalcium phosphate as described by the referee be adopted as tentative.

Approved.

(2) That further study be made of the electrolytic method for the determination of lead.

Approved.

(3) That further study be made of volumetric methods for the determination of carbon dioxide in baking powder.

Approved.

(4) That further collaborative study be made of methods for the determination of fluorine in baking powder.

Approved.

CHEMICAL REAGENTS.

It is recommended—

That the work on reagents be continued as formerly and that the members of the association cooperate as fully as possible with the referee in maintaining the high standards of purity and dependability for chemicals.

NON-ALCOHOLIC BEVERAGES.

It is recommended—

That the subject of flavoring extracts and non-alcoholic beverages be combined under one heading, "Flavors and Non-alcoholic Beverages".

Approved.

EGGS AND EGG PRODUCTS.

It is recommended—

That a referee be appointed to study collaboratively the methods proposed for the examination of eggs and egg products[1].

DRUGS.

ACETYLSALICYLIC ACID.

It is recommended—

(1) That the method for the preparation of acetylsalicylic acid for the determination of the melting point[2] be adopted as a tentative method.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 6: 5.
[2] *Ibid.*, 5: 582.

(Determination of the melting point is made in accordance with directions of the U. S. P.)

Approved.

(2) That the tentative method for the quantitative determination of free salicylic acid[1] be considered by the referee next year with a view to its adoption as official.

Approved.

(3) That the tentative iodine method for the determination of total salicylates[1] be studied by the incoming referee with a view to its adoption as an official method.

Approved.

(4) That the bromine method for the determination of total salicylates[1] be studied by the incoming referee with a view to its adoption as an official method.

Approved.

(5) That the double titration method for the determination of acetylsalicylic acid[2] be studied by the incoming referee with a view to its adoption as an official method.

Approved.

(6) That further study be made of methods for the determination of free acetic acid[2].

Approved.

(7) That the problem of determining acetylsalicylic acid in the presence of possible interfering substances be given consideration by next year's associate referee.

Approved.

PHENOLPHTHALEIN.

It is recommended—

That further study be made of the methods submitted for the examination of phenolphthalein.

Approved.

CAMPHOR.

It is recommended—

That the methods suggested for the determination of camphor in pills and tablets[3] be further studied during the coming year.

Approved.

MONOBROMATED CAMPHOR.

It is recommended—

That the tentative methods adopted at the 1921 meeting[4] be made the subject of collaborative study during the coming year.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 582.
[2] *Ibid.*, 583.
[3] *Ibid.*, 544.
[4] *Ibid.*, 587.

MERCURY.

It is recommended—

That an associate referee be appointed to study the methods for the examination of mercurous chloride, mercuric chloride and mercuric iodine, already reported to the association, or such methods as may be available elsewhere for the purpose of developing a satisfactory method.

Approved.

TURPENTINE.

It is recommended—

(1) That the fuming sulfuric acid method[1] as modified by the referee be adopted as tentative.

Approved.

(2) That the sulfuric-nitric acid method[1] as published in *The Journal* be adopted as tentative.

Approved.

(3) That the method of Grotlisch and Smith[2] for the determination of coal tar, oils and turpentine be studied.

Approved.

ALKALOIDS.

SEPARATION OF QUININE AND STRYCHNINE.

It is recommended—

That the methods submitted[3] be further studied.

PHYSOSTIGMA, FLUID EXTRACT OF HYOSCYAMUS, OINTMENT OF STRAMONIUM, BELLADONNA OINTMENT, BELLADONNA LINIMENT, IPECAC AND ATROPINE.

It is recommended—

(1) That the method for the assay of physostigma and its preparations, and that for fluid extract of hyoscyamus[4], as submitted by the associate referee, be referred to the chairman of the appropriate committee of the U. S. P. Revision Committee for consideration in connection with the revision of the U. S. P., and further that these methods remain tentative until such time as they appear in the Pharmacopœia.

Approved.

(2) That further study be made of the methods for the assay of ointment of stramonium, belladonna ointment, belladonna liniment, and ipecac.

Approved.

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 552.
[2] *J. Ind. Eng. Chem.*, 1921, **13**: 791.
[3] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 567.
[4] *Ibid.*, 568.

(3) That the methods for the determination of atropine in tablets be studied.

Approved.

STRYCHNINE.

It is recommended—

(1) That the method for the assay of strychnine in tablets[1], including the volumetric method, be adopted as an official method. (Second action as an official method.)

Adopted.

(2) That the method for the assay of strychnine in liquids[2], including the volumetric method, be adopted as an official method. (Second action as an official method.)

Adopted.

MORPHINE, CODEINE AND DIACETYLMORPHINE.

It is recommended—

(1) That the methods submitted for the qualitative and quantitative determination of morphine, codeine and diacetylmorphine[3], be adopted as official. (First action as official methods.)

Approved.

PROCAINE.

It is recommended—

That the two methods submitted[4] be adopted as official. (First action as an official method.)

Approved.

MEDICINAL PLANTS.

It is recommended—

(1) That a study of volume weight of medicinal plants be continued with the assistance of collaborators.

Approved.

(2) That a further study be made of the sublimation of plant products.

Approved.

SANTONINE.

It is recommended—

(1) That the tentative method for the detection of santonine in wormseed[5] be studied by collaborators with a view to making it official.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 301.
[2] *Ibid.*, 300.
[3] *J. Assoc. Official Agr. Chemists*, 1922, 5: 150.
[4] *Ibid.*, 590.
[5] *Ibid.*, 557.

POLLEN GRAINS.

It is recommended—

(1) That the method for the use of pollen grains as the means of identification of plants and plant products[1] be further studied.

Approved.

BITTER TONIC AND LAXATIVE DRUGS.

It is recommended—

(1) That the gravimetric method evolved for assaying the anthraquinone drugs[2] be given a more exhaustive study during the coming year.

Approved.

(2) That conjointly with the study of gravimetric assay, the collaborative work be extended to the colorimetric determination.

Approved.

(3) That the method for estimating aloin[3] be submitted to the association for study and criticism.

Approved.

ARSENICALS.

It is recommended—

(1) That the qualitative and quantitative methods[4] submitted be adopted as official. (First action as an official method.)

Approved.

(2) That the designated modification of the quantitative method[5] be adopted as a tentative method.

Approved.

(3) That further study of organic sulfur and toxicity tolerance of arsphenamine be discontinued.

Approved.

SANDALWOOD OIL.

It is recommended—

That the methods submitted and studied by C. W. Harrison for the determination of the acetyl value of sandalwood oil[6] be further studied.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1921, 5: 157.
[2] *Ibid.*, 1922, 5: 575.
[3] *Ibid.*, 580.
[4] *Ibid.*, 526.
[5] *Ibid.*, 528.
[6] *Ibid.*, 545.

SILVER PROTEINATES.

It is recommended—

That further work be carried out on Method 3[1].

Approved.

ALCOHOL IN DRUGS.

It is recommended—

That the method for the determination of alcohol in drugs[2] be further studied.

Approved.

CHLOROFORM.

It is recommended—

That the method for the determination of chloroform[3] be further studied.

Approved.

CINCHONA ALKALOIDS.

It is recommended—

That further study be made of the separation of the principal cinchona alkaloids[4].

Approved.

METHYLENE BLUE.

It is recommended—

That the iodine method for the determination of methylene blue be adopted as tentative.

Approved.

PHENYLCINCHONINIC ACID (ATOPHAN).

It is recommended—

That the method of assay reported by the referee be studied collaboratively.

Approved.

CHLORAMINE PRODUCTS.

It is recommended—

That further study be made of the tests and methods reported by the referee.

Approved.

DIMETHYLAMINOANTIPYRINE (PYRAMIDON).

It is recommended—

That the extraction method and the precipitation methods reported by the referee be further studied.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 543.
[2] *Ibid.*, 530.
[3] *Ibid.*, 539.
[4] *Ibid.*, 594.

REPORT OF COMMITTEE C ON RECOMMENDATIONS OF REFEREES.

By R. E. DOOLITTLE (1625 Transportation Building, Chicago, Ill.), *Chairman*.

[Food preservatives (saccharin), coloring matters in foods, metals in foods (arsenic), fruits and fruit products (pectin in fruits and fruit products, moisture in dried fruit), canned foods, cereal foods, limits of accuracy in the determination of small amounts of alcohol, vinegars, flavoring extracts, meat and meat products (separation of meat proteins), gelatin, spices and other condiments, determination of shells in cacao products, methods for the examination of cacao butter, coffee, tea, and nitrogen in foods.]

FOOD PRESERVATIVES.

SACCHARIN.

It is recommended—

That the studies of methods for the determination of saccharin be continued.

Approved.

COLORING MATTERS IN FOODS.

It is recommended—

(1) That the tentative methods for the separation and identification of soluble coloring matters and their lakes[1] be studied during the coming year.

Approved.

(2) That the tentative methods for the separation and identification of oil-soluble dyes[2] be studied during the coming year.

Approved.

METALS IN FOODS.

It is recommended—

That the zinc-iron precipitation method, as described by the referee, for the determination of tin be studied collaboratively during the coming year.

Approved.

ARSENIC.

It is recommended—

(1) That the Gutzeit method for arsenic[3] be modified in the following manner to permit the use of hydrochloric acid as an alternate acid in the determination:

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 131, 136.
[2] *Ibid.*, 132, 136.
[3] *Ibid.*, 147.

(a) Chapter **XI, 1 (b)** add "or hydrochloric acid, arsenic-free (1 to 1)", making the sentence read "**(b)** Sulphuric acid, arsenic-free (1 to 2) or hydrochloric acid, arsenic-free (1 to 1)".

(b) Chapter **XI, 4,** line 3 after the phrase "and add 20 cc. of the dilute sulphuric acid" insert "or 20 cc. of the 1 to 1 arsenic-free hydrochloric acid", making the sentence read "and add 20 cc. of dilute sulphuric acid or 20 cc. of the 1 to 1 arsenic-free hydrochloric acid".

Approved.

(2) That the tentative Gutzeit method for the determination of arsenic as revised be adopted as an official method. (First action as an official method.)

Approved.

FRUITS AND FRUIT PRODUCTS.

PECTIN IN FRUITS AND FRUIT PRODUCTS.

It is recommended—

(1) That further studies be made by the method of Carré and Haynes for the determination of calcium pectate[1] and the method of Wichmann and Chernoff for the determination of pectic acid[2] to determine the composition of pectin.

Approved.

(2) That the methods for preparation of sample, alcohol precipitate, pectic acid, ash, sulfur in ash, total sulfur and water-insoluble solids[3] submitted at the 1921 meeting for the determination of pectin in fruits and fruit products be studied by the referee during the coming year.

Approved.

MOISTURE IN DRIED FRUITS

It is recommended—

(1) That the following method for the determination of moisture in all dried fruits by drying in vacuo be adopted as an official method. (Second action as an official method.)

Weigh 5–10 grams of the sample into a metal dish about 8.5 cm. in diameter, provided with a cover, breaking down any large lumps. Dry in vacuo at 70°C. for 12 hours at as low a pressure as possible, not to exceed 4 in. (100 mm.) of mercury. During the drying admit to the oven a slow current of air, about 2 bubbles per second, dried by bubbling through concentrated sulfuric acid. The metal dish must be placed in direct contact with the metal shelf of the oven. Replace cover, cool in a desiccator and weigh. Disregard any temporary drop of oven temperature which may occur during the fore part of the drying period owing to rapid evaporation of water. With raisins and fruit similarly rich in sugar use about 5 grams of sample and about 2 grams

---

[1] *Biochem. J.*, 1922, **16**: 60.
[2] *J. Assoc. Official Agr. Chemists*, 1922, **6**: 36.
[3] *Ibid.*, 35.

of finely divided asbestos dried with the dish. Moisten with hot water, mix sample and asbestos thoroughly, evaporate on the water bath barely to dryness and complete drying as above.

Approved.

(2) That the following method for the determination of moisture in dried apples only be continued as a tentative method:

Weigh 5–10 grams of the sample into a metal dish about 8.5 cm. in diameter, provided with a cover, breaking down any large lumps, and dry for 4 hours in an oven at the temperature of boiling water. Replace cover, cool in a desiccator and weigh. Place dishes on shelves and not on oven bottom. The oven should have a vent on top to secure ventilation and the temperature should not be below 96°C.

Approved.

(3) That further consideration be given to the determination of moisture in dried fruits by methods based upon an entirely different principle.

Approved.

CANNED FOODS.

It is recommended—

That studies of the methods for the microanalysis of tomato pulp, catsup, purée, sauce and paste as corrected[1] at the 1921 meeting be continued.

Approved.

CEREAL FOODS.

It is recommended—

(1) That the tentative method[2] adopted at the 1921 meeting for the determination of fat in baked cereal products be made official. (First action as an official method.)

Approved.

(2) That the method for the determination of chlorine in bleached flours as given in the referee's report be adopted as a tentative method.

Approved.

(3) That further studies be made of the methods for the determination of chlorine in bleached flour.

Approved.

(4) That the official method for the determination of moisture in wheat flour[3] be amplified as follows:

Dry 2 grams of flour in a tared metal dish about 40 cm. in diameter by 25 cm. high, and provided with a tight fitting cover, to constant weight in a vacuum oven at a

[1] *J. Assoc. Official Agr. Chemists*, 1922, 6: 49.
[2] *Ibid.*, 63.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 167.

pressure of not to exceed 5 cm. of mercury, and at a temperature of 100°C. Cool the dish in a desiccator, and weigh immediately after the dish and contents reach the temperature of the air in the laboratory.

(First action as change in an official method.)

Approved.

(5) That the official method for the determination of ash in wheat flour[1] be amplified as follows:

Ignite a crucible; when cooled, weigh, and rapidly weigh into it 5 grams of the flour. Ignite in a muffle at approximately 550°C. taking care that no portion of the muffle becomes sufficiently hot to fuse the ash. A light-gray, fluffy ash should result. Cool the crucible and contents in a desiccator, and weigh immediately after it reaches the temperature of the laboratory air.

(First action as change in an official method.)

Approved.

(6) That the official method for the determination of protein in wheat flour[1] be amplified to cover the same determination in wheat in order to provide that the percentage of nitrogen in wheat as well as flour shall be multiplied by 5.7 to obtain the percentage of protein. (First action as an official method.)

Approved.

LIMITS OF ACCURACY IN THE DETERMINATION OF SMALL AMOUNTS OF ALCOHOL.

It is recommended—

That the studies of the methods for the determination of small amounts of alcohol be continued.

Approved.

VINEGARS.

It is recommended—

(1) That the method for the physical examination of vinegar[2] be made official. (Second action as an official method; first action taken in 1919.)

Approved.

(2) That the methods[3] for the determination of alcohol, reducing sugars, polarization and color, be studied by the referee during the coming year.

Approved.

(3) That methods for the determination of sulfates and barium be considered by the referee during the coming year.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 167.
[2] *Ibid.*, 191.
[3] *Ibid.*, 191–195.

FLAVORING EXTRACTS.

It is recommended—

(1) That the subjects of "Flavoring Extracts" and "Non-Alcoholic Beverages" be combined under one heading, "Flavors and Non-Alcoholic Beverages".

Approved.

(2) That the referee give consideration to methods for the analysis of non-alcoholic flavors, as for example the determination of orange oil and lemon oil in mineral oil, cottonseed oil, etc.

Approved.

(3) That the referee give consideration to the method adopted at the 1919 meeting of the association, as official, first action, for the determination of alcohol in orange and lemon extracts consisting only of alcohol, oil and water[1] to the end that final action may be taken on the method at the 1923 meeting.

Approved.

MEAT AND MEAT PRODUCTS.

It is recommended—

That the tentative method for the determination of sugar in meat and meat products[2] and the modifications of the method suggested by the referee in 1921[3] be studied during the coming year.

Approved.

SEPARATION OF MEAT PROTEINS.

It is recommended—

(1) That further work be done on the relation of the concentration of acid and protein to the coagulation by salt of proteins of meat soluble in cold water[4].

Approved.

(2) That zinc sulfate be compared with ammonium and sodium sulfates for the separation of meat proteins[4].

Approved.

(3) That further work be done with the sodium chloride and tannic acid method for the determination of the amino-acid and extractive nitrogen[4] to determine all the conditions necessary to give comparable results.

Approved.

---

1 *J. Assoc. Official Agr. Chemists*, 1921, 4: 472, 579.
2 *Assoc. Official Agr. Chemists, Methods*, 1920, 213.
3 *J. Assoc. Official Agr. Chemists*, 1922, 6: 72.
4 *Ibid.*, 76–85.

GELATIN.

It is recommended—

(1) That the present tentative method[1] for the determination of copper be continued as a tentative method.

Approved.

(2) That further study be made of the tentative method for the determination of zinc[2] and the alternate method for copper and zinc[2].

Approved.

SPICES AND OTHER CONDIMENTS.

It is recommended—

(1) That the following details for the determination of crude fiber in prepared mustard be adopted tentatively:

Weigh 10 grams of the sample and transfer to an 8 ounce nursing bottle with 50 cc. of strong alcohol, stopper and shake vigorously. Add 40 cc. of ethyl ether, shake and let stand about 5 minutes with occasional shaking. Centrifuge and decant off the alcohol-ether mixture. Treat twice more with 40 cc. portions of ether, shaking, centrifuging and decanting as before. Rest the bottle on its side for a short time, without heat, to allow the ether largely to evaporate. Transfer the material to a 1000 cc. Erlenmeyer flask using 200 cc. of the boiling dilute sulfuric acid and proceed as directed in VII, 66[3].

Or treat the sample with the alcohol and ether in a small beaker; transfer to a hardened 11 cm. filter paper, wash several times with ether, and finally transfer to a 1000 cc. Erlenmeyer flask with 200 cc. of the boiling dilute sulfuric acid.

Approved.

(2) That during the coming year the referee consider the above described method in comparison with that printed in the Methods of Analysis, A. O. A. C.[4], for crude fiber in prepared mustard, for the purpose of determining if both are acceptable methods or if either should be dropped.

Approved.

(3) That the methods submitted by the referee in his report for the examination of salad dressings be subjected to further study during the coming year, employing samples differing from those used by containing a small proportion of oil and a binding material.

Approved.

(4) That the method for the determination of lecithin phosphoric acid in salad dressings given by the referee in his report be further studied together with any available modification thereof.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 344.
[2] *Ibid.*, 345
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 98.
[4] *Ibid.*, 262.

CACAO PRODUCTS.

DETERMINATION OF SHELL.

It is recommended—

That the tentative method for the determination of cacao shells in cacao products[1] be further studied during the coming year together with the supplemental methods outlined by the referee this year for the preparation for microscopic examination of sweet and sweetened milk chocolates.

Approved.

METHODS FOR THE EXAMINATION OF CACAO BUTTER.

It is recommended—

(1) That the following critical temperature of dissolution in acetic acid test be adopted as a tentative method:

REAGENTS.

(a) Glacial acetic acid, as free as possible from water.

(b) 0.1N potassium hydroxide solution.

APPARATUS.

Insert a thermometer reading to 0.1°C. into a cork that fits a 6x¾ inch test tube. The thermometer should extend far enough into the tube that the bulb will be covered by 10 cc. of liquid. Place the test tube in a larger tube (4x1¼ inch) containing glycerine and hold firmly in place with a cork having a groove cut in the side to equalize the pressure when heat is applied.

DETERMINATION.

Filter a portion of the sample to be examined through a dry filter paper in an oven where a temperature of about 110°C. is maintained, to remove traces of moisture. Allow the filtered sample to cool until barely warm, and weigh (a pulp balance is accurate enough) 5 grams of the sample and 5 grams of the acetic acid reagent (a) into the test tube. Insert the cork holding the thermometer and place the test tube in the glycerine bath. Heat and shake the apparatus frequently until a clear solution of the fat and acetic acid is obtained. Allow the solution to cool with constant shaking without removing from the glycerine bath. Note the temperature at which the first sign of turbidity appears. Make a similar test with the same acetic acid on a sample of pure cacao butter. Free fatty acids lower the turbidity temperature. A correction must therefore be made for the acid value of the sample.

CORRECTION FACTOR.

If the strength of the acetic acid reagent is such that the turbidity temperature of the pure cacao butter is, approximately, 90°C. one unit of acid value will cause a reduction of 1.4 degrees in the critical temperature of dissolution. If the turbidity temperature is approximately 100°C., one unit of acid value will cause a reduction of 1.2 degrees. For intermediate temperatures the reduction is proportional.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 6: 99.

CORRECTED CRITICAL TEMPERATURE OF DISSOLUTION.

Determine the acid value (mg. of potassium hydroxide required to neutralize the free fatty acids in 1 gram of the sample) of both the sample and the pure cacao butter as directed under XXII, 30[1]. Multiply the acid value by the correction factor and add the result to the observed turbidity temperature. The figure obtained is the true critical temperature of dissolution. If the true critical temperature of dissolution of the sample is lower by more than 2 degrees than that of the pure cacao butter, adulteration with coconut, palm kernel, cottonseed oils or stearines, corn oil, peanut oil or other vegetable oils is indicated.

Approved.

(2) That the following acetone-carbon tetrachloride test be adopted as a tentative method:

REAGENT.

A mixture of equal parts of acetone and carbon tetrachloride.

DETERMINATION.

Dissolve 5 cc. of the warm fat, which has been previously filtered through dry filter paper in an oven at about 110°C. to remove traces of moisture, in 5 cc. of the acetone-carbon tetrachloride reagent in a test tube. Allow the solution to stand in ice water for 20–30 minutes. Run a blank on a sample of pure cacao butter at the same time. If hydrogenated oil, tallow, oleostearine or paraffin is present a white flocculent precipitate will soon appear. If the water is cold enough, cacao butter may solidify. If a precipitate is formed remove the sample from the ice water and allow to remain at room temperature for a time. Solidified cacao butter will soon melt and go into solution but if the precipitate is due to any of the above-mentioned possible adulterants a much longer time will be required for it to go into solution.

Approved.

(3) That the studies of the critical temperature of dissolution in acetic acid and acetone-carbon tetrachloride tests be continued.

Approved.

COFFEE.

It is recommended—

That the studies of the acids of coffee be continued.

Approved.

TEA.

It is recommended—

(1) That the Bailey-Andrew method for the determination of caffeine in tea[2] be adopted as an official method. (Second action as an official method.)

Approved.

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 250.
[2] *J. Assoc. Official Agr. Chemists*, 1922, 5: 292.

(2) That the following method for the determination of water extract in tea be adopted as an official method. (First action as an official method.)

To 2 grams of the ground sample in a 500 cc. graduated flask add 200 cc. of hot water and boil over a low flame for 1 hour, rotating occasionally. The flask should be closed with a rubber stopper through which passes a glass tube 30 inches long for a condenser. Boil very slowly so that no steam escapes from the top of the air condenser. Cool, dilute to volume, mix thoroughly and filter through a dry filter paper. Take an aliquot of 50 cc. and evaporate to dryness over a steam bath. Then place in oven and heat at 100°C. for 1 hour, cool and weigh.

Approved.

(3) That suggestions for further studies on tea be left to the incoming referee.

Approved.

NITROGEN IN FOODS.

It is recommended that this subject be discontinued.

Approved.

THIRD DAY.

FRIDAY—AFTERNOON SESSION.

REPORT OF COMMITTEE TO COOPERATE WITH THE REVISION COMMITTEE OF THE UNITED STATES PHARMACOPŒIA.

Shortly after the last annual meeting, the chairman advised E. Fullerton Cook, Chairman of the United States Pharmacopœia Revision Committee, of the appointment by this association of a committee of five to cooperate with the committee of revision dealing with matters having to do with methods of analysis, physical constants and other analytical features. His attention was also called to the fact that the A. O. A. C. methods of analysis contained directions for analyzing drugs which are different in some respects from those contained in the present Pharmacopœia.

The suggested plan of placing copies of monographs at the disposal of the members of the committee for criticism appealed to Chairman Cook and the monographs were sent to the members of our committee. The criticisms were submitted to the A. O. A. C. chairman, assembled and transmitted to the chairman of the Revision Committee.

In April a communication was addressed to Chairman Cook, criticizing certain features contained in the monograph submitted and making suggestions.

In this communication the committee discussed the following subjects: Brevity of statements consistent with clarity and definiteness; suitable sub-headings to enable workers to find at a glance what is wanted; the necessity of stating definitely the condition of a substance used in making tests; avoidance of duplication; consistency in using the final e; assay methods for acetanilid and antipyrine; a standardization of connectives so that they will have a definite meaning wherever used; avoidance of the use of indefinite words and loose phrases; replacement of such phrases as "should contain" with the word "contains"; avoidance of necessity of analyst interpreting loose statements; the inadequacy of the tests proposed for detecting certain forms of adulterants; recasting of monographs of botanicals to bring them into harmony with the monographs on other subjects; and the desirability of discontinuing the centigrade abbreviation when this is practically the only scale used.

Monographs received later did not seem to contain anything of a material character, not covered by the communication of your committee. These monographs are in tentative form for criticism and revision.

Your chairman discussed at length the idea of a general uniform working temperature for laboratory work in which temperature is involved, such as alcohol tables, specific gravities, optical readings, refractive indices, refractometer observations, etc. He also communicated with F. M. Farmer, Chairman of the Sub-committee on Specific Gravities of the American Society for Testing Materials.

The more the subject was discussed and considered, the more complex and difficult the probabilities of getting together on a uniform temperature became and agreement on such a temperature seemed very remote.

In order to obtain an expression from the members of this association and subscribers to *The Journal* of the association, a questionnaire was sent to all persons or institutions of record and also to a number of other persons known to be interested in this work. About 1300 questionnaires were sent out; 381 replies have been received to date. The questionnaire follows:

UNIFORM TEMPERATURE FOR MAKING DETERMINATIONS AND A VOTE ON THE U. S. P. *vs.* A. O. A. C. ALCOHOL TABLES.

At the last meeting of the A. O. A. C., criticism was made of the A. O. A. C. and U. S. P. alcohol tables. The sentiment appeared to be in favor of the A. O. A. C. tables. The Chairman of the Committee to Cooperate with the U. S. Pharmacopœial Committee on Revision, appointed at the last meeting, has discussed the question considerably with the conviction that a conclusion is not so easily arrived at. The committee itself is divided; two are in favor of the A. O. A. C. alcohol tables and two in favor of the U. S. P. alcohol tables. The chairman has not yet been called upon to cast his vote but favors the 20°/4° tables from a purely scientific point of view, yet trade conditions play an important part and must be considered.

In view of the unsatisfactory outcome so far, the chairman is submitting the matter to the A. O. A. C. membership for discussion, criticism and a vote.

It is conceded that the most convenient temperature for making routine observations is the laboratory temperature, but this temperature varies considerably from time to time and in different sections of the country. A compromise temperature should be agreed on.

The A. O. A. C. tables are based on the Bureau of Standards table 20°/4°, and represent true specific gravities, whereas the U. S. P. tables are based on the Bureau of Standards tables 15.56°/15.56°, and are apparent specific gravities, barometer at 760 mm. with 50% air saturation. The Bureau of Standards, so far as your chairman has been able to ascertain, has not committed itself to any temperatures for alcohol tables or for determining specific gravities of alcoholic mixtures, but has adopted 20° as the temperature for standardizing apparatus. 20°/4° is considered the more scientific, but 15.56°/15.56° is more largely used in the industries and by industrial chemists and 60°F./60°F. is written into the Internal Revenue law dealing with alcohol products. The Gauger's Manual tables are also based on this temperature.

The question of a uniform temperature for alcohol tables is important in case of per cent by volume, but percentage of alcohol by weight is independent of temperature. It is true that specific gravities of alcoholics may be made at any temperature desired but uniformity is highly desirable and the alcohol tables should be based on a uniform temperature.

The A. O. A. C. methods of analysis provide that specific gravities, whenever practicable, be determined on the basis of 20°/4° and that refractive indices and optical rotations be made at 20° whenever practicable. This certainly makes for uniformity.

The U. S. Interdepartmental Committee on Paint Specification Standardizations (consisting of representatives of the War, Navy, Agricultural, Interior, Post Office, Treasury and Commerce Departments; the Railroad Administration; the Panama Canal; and the War Service Committee of the Paint Manufacturers Association of the United States) has adopted 15.5°/15.5° for linseed oil and oil of turpentine.

U. S. Pharmacopœial optical rotations are to be made at 25°; refractive indices at 20°; and specific gravities, unless otherwise provided, at 25°/25°. See Page LII of the present Pharmacopœia.

F. M. Farmer, Chairman of the Subcommittee on Specific Gravity of the American Society for Testing Materials, writes:

> On the question of temperature there are so many standards already established in industry that it seems hopeless to get standardization on any one temperature. I am proposing therefore that our committee simply recommend that where there is no particular reason for adopting other values, the standard temperature of reference for the material be 25° and for the water 4°.

In order that the committee may have your views, please answer the following questions, etc., and return in enclosed franked envelope.

1. Are you in favor of the A. O. A. C. alcohol tables? . . . .
2. Are you in favor of the U. S. P. 9th Revision, alcohol tables? . . ..
3. What single *working temperature* do you consider best for determining specific gravities, optical readings, refractive indices, immersion refractometer readings, etc.?

Suggestions and comments:

Your chairman presented the results obtained by the committee at a general meeting of the American Pharmaceutical Association last September, the idea being to bring the information so far obtained to the attention of all interested at the earliest practical date. This course was taken with the advice of President Veitch. The report was printed in the journal of the association[1]. A short notice of the work of the committee was also printed in the *Journal of Industrial and Engineering Chemistry*[2]. In each communication a request was made that all interested in these matters communicate their views to your chairman as early as possible. It is with extreme reluctance that he reports that only one vote has been received in response to the information published in these two journals.

The total number of votes received to date is 382, tabulated as follows:

Results of Vote on Alcohol Tables.

In favor of A. O. A. C. tables	287
Not in favor of	35
Not voting	60
In favor of U. S. P. 9th Revision	40
Not in favor of	184
Not voting	158

[1] *J. Am. Pharm. Assoc.*, 1922, 11: 859.
[2] *J. Ind. Eng. Chem.*, 1922, 14: 988.

The results of a vote on best working temperature show that 261 favor 20°; 83 favor 25° and 14 favor 15.5.

These results are so different from what was anticipated that the committee feels greatly encouraged.

The report presented at the American Pharmaceutical Association meeting has been mimeographed by Chairman Cook and sent to the members of the U. S. P. committee, but no definite action has been taken so far as is known to your chairman.

The United States Pharmacopœial convention in its adoption of general principles to govern in revising the Pharmacopœia, unfortunately stipulated that 25° should be used except in the alcohol tables. Some of the members of the Committee of Revision are definitely in favor of the 20° temperature, but do not see how it is possible to adopt this temperature in view of the fact that the convention itself voted 25°.

The vast majority of those voting favor the A. O. A. C. alcohol tables, but this vote may not be representative and therefore no conclusion is drawn at present.

The vote on Question 3, covering the best temperature for making determinations, is very definitely in favor of 20°, nearly 3 to 1, as against all other temperatures.

To satisfy a natural curiosity concerning the personnel of this vote a partial list of representative voters, selected at random, is given.

Partial list of votes on best working temperature.

Allyn, L. B. Analytical Laboratories, Westfield, Mass.	20°
American Sugar Refining Co., New York	20
American Tobacco Co., New York	20
Antoine Chiris Co., Essential Oils, New York	20
Armour & Co., Packers and Manufacturers of Foods and Drugs, Chicago	20
Ash, Charles S., Analytical Laboratory, San Francisco	15.56
Bartlett, J. M., Experiment Station, Orono, Me.	20
Browne, C. A., The New York Sugar Trade Laboratory, New York	20
Bureau of Chemistry, Washington, D. C.	20
Bureau of Standards, Washington, D. C.	20
California State Board of Health, Berkeley	20
Campbell Co., Joseph, Soup Manufacturers, Camden, N. J.	25
Department of Health, Canada	20
Doolittle, R. E., Editor A. O. A. C. Methods, Chicago	20
General Chemical Co., Chemical Manufacturers, San Francisco office	20
Gorton Pew Fisheries, Gloucester, Mass.	20
Great Western Sugar Co., Denver, Colo.	20
Heinz, H. F. Co., Pickle Manufacturers, Pittsburgh	20
Hilton, S. L., Druggist, President of the American Pharmaceutical Association 1922, Washington, D. C.	20
Iowa State Dairy and Food Commission, Des Moines	20
Johns, C. O., Standard Oil Co., New York	20
Langley & Michaels, Wholesale and Manufacturing Druggists, San Francisco	20

Lehn & Fink, Wholesale and Manufacturing Druggists, New York	20
Loomis, H. M., National Canners Association, Washington, D. C.	20
Massachusetts State Board of Health, Boston	20
National Biscuit Co., Chicago	20
Pacific American Fisheries Laboratories, South Bellingham, Wash.	15.5
Parke, Davis & Co., Pharmaceutical Manufacturers, Detroit, Mich.	25
Powers, Weightman & Rosengarten, Chemical Manufacturers, Philadelphia	25
Proctor & Gamble, Soap Manufacturers, Cincinnati	25
Royster, F. S., Guano Co., Fertilizers, Norfolk, Va.	20
Sears, Roebuck & Co., Mail Order and Manufacturers, Chicago	20
Sharp & Dohme, Pharmaceutical Manufacturers, Baltimore	20
Sherwin Williams Co., Paint Manufacturers, Cleveland	20
Solvay Process Co., Heavy Chemical Manufacturers, Syracuse, N. Y.	20
Sprague Warner & Co., Wholesale Food Manufacturers, Chicago	25
United Drug Co., Retailers and Drug Manufacturers, Boston	20
University of Montreal	20
Veitch, F. P., President A. O. A. C.	20
Warner, Wm. R. & Co., Drug Manufacturers, New York	25
Woodman, A. G., Massachusetts Institute Technology, Boston	20

The vote as given shows practically the same ratio as the entire vote and is 3 to 1 in favor of 20°, as against all other temperatures.

Other chemists than those in the United States are annoyed by the multiplicity of temperatures prescribed by various authorities for making observations. The same condition exists in other countries and some efforts are being made to obtain uniformity. F. Auerbach, a member of a Committee for Physical Constants[1], calls attention to the chaos existing in Germany. After studying conditions the committee concluded that 20° is best suited for a general working temperature. This "normal temperature", as Auerbach calls it, is to be used for standardizing apparatus, tools, electric cells, optical readings, specific gravities, etc., unless there are some definite reasons for selecting another temperature.

Your committee feels that the outlook for ultimately agreeing on 20° as a general working temperature by the vast majority of scientists and industries is excellent and recommends the work of the committee be continued.

Respectfully submitted,

L. F. Kebler, A. R. Bliss,
H. C. Lythgoe, W. S. Hubbard.
H. C. Fuller,

Committee to Cooperate in Revision of the U. S. Pharmacopœia.

Approved.

A motion that this committee be continued was made, seconded and carried.

[1] *Pharm. Z.*, 1922, 67: 303.

REPORT OF REPRESENTATIVES ON THE BOARD OF GOVERNORS OF THE CROP PROTECTION INSTITUTE OF THE NATIONAL RESEARCH COUNCIL.

In the last report, the objects of the Crop Protection Institute were outlined briefly and need not be repeated. Without special mention it might not be realized that "crop" is interpreted rather broadly by the institute to include animal as well as vegetable products of the farm. In fact, a part of the necessary funds is already available for an investigation of the control of the ox warble.

A method of procedure by which scientific investigations could be conducted for the industrial organizations, by direction of the institute, has been determined.

This was a matter requiring very careful attention in order that the contemplated service should not in any way embarrass other public-service activities, for example, inspection or control work, with which this association is so largely concerned.

Fortunately, a conference was made possible with the Federal Insecticide Board, and invaluable suggestions were received from those who have had long experience with proprietary articles. Suggestions and criticisms were so carefully considered and the decisions so universally endorsed that there would seem to be no reason for difficulties to arise concerning the interests of public-service organizations dealing with similar materials.

It can be imagined that if, for the purpose of investigation, a proprietary material is submitted by an industrial concern, with a statement of its composition and expected usefulness, an awkward situation might arise as to whether claims were justified or not. It seems appropriate, therefore, to quote the following section of the method of procedure:

> It is understood that the Institute will at all times conduct its investigations and reach its findings in full understanding with Federal and State officials directly concerned.

Three sulfur-producing companies, by cooperating in furnishing funds for basic investigations of the value of sulfur in combatting crop pests, have made possible full-time fellowships for well-trained men during a period of two years.

Investigations have also been arranged to determine the comparative value of dry chemicals for the treatment of cereals for smut eradication.

Orchard dusting work done in 1921 was reported by the institute in Bulletin No. 2, February 1922. This research has been continued.

Other projects under consideration concern lime, miscible oils, sublimed sulfur, nickel compounds and cobalt compounds.

Now that methods of procedure have been determined, the institute is in a position to give satisfactory attention to problems which are of sufficient interest for industry to provide funds for their investigation. Intelligent supervision and laboratory equipments are available.

BURT L. HARTWELL,
H. J. PATTERSON.

Approved.

REPORT OF SECRETARY-TREASURER.

By W. W. SKINNER (Bureau of Chemistry, Washington, D. C.), *Secretary-Treasurer.*

The report of the secretary-treasurer this year includes a brief review of the activities of the Executive Committee of the association since the date of the 1921 convention. The purpose of this is to inform the members and also to provide for the insertion in the proceedings of a record of the Executive Committee's work, since this committee to a certain extent represents the association in the intervals between its regular meetings.

Early in 1922 the association suffered an irreparable loss in the death of Dr. William Frear of Pennsylvania, one of its most active and honored members. His death created a vacancy in the Committee to Cooperate with Other Committees on Food Definitions and in the Committee to Cooperate with the American Society for Testing Materials on the Subject of Agricultural Lime. The Executive Committee filled these vacancies by appointing E. M. Bailey of Connecticut a member of the Committee to Cooperate with Other Committees on Food Definitions, and J. B. Weems of Virginia, a member of the Committee to Cooperate with the American Society for Testing Materials on the Subject of Agricultural Lime. A vacancy in the position of Referee on the Determination of Shells in Cacao Products, caused by the resignation of B. H. Silberberg, was filled by the appointment of V. A. Pease, of the Bureau of Chemistry, Washington, D. C.

At the meeting last year it was reported that the suit brought against the association by the Williams & Wilkins Co. of Baltimore, Md., former publishers of *The Journal*, had been dropped by that firm and the decision as to the action which the association should take in the matter was left to the Executive Committee with power to act. As had been anticipated, it soon became necessary to make a decision. A bill for $500 for legal services was presented by the attorneys who had been

engaged to represent the association in that suit—Messrs. Frank, of Frank, Emory and Beeuwkes of Baltimore and Sherier, of Leckie, Cox and Sherier, of Washington—and these gentlemen began to press for payment. The members of the Executive Committee felt that a charge of $500 for the services rendered was excessive, but as this bill was submitted after these attorneys had been informed of the status of the association's finances and requested to make their charge as low as possible, there seemed to be little probability that they could be prevailed upon to modify it. Nevertheless an attempt was made to secure a reduction. Messrs. Frank and Sherier contended, however, that the bill was a most reasonable one and that it would have been larger except for the considerations which had already been brought to their attention. Under the circumstances, the Executive Committee decided that the best and practically the only thing to do was to authorize the payment of this bill and to consider the whole matter closed. This was done by a unanimous vote of the committee and the bill was paid in part from dues and in part from funds credited to the account of *The Journal.*

The secretary has found that there seems to be an impression on the part of some that membership in the association, as represented by the payment of dues, carries with it a subscription to *The Journal.* Such is not the case, and as misunderstandings of this kind becloud the significance of the dues and increase the difficulty of financing *The Journal,* a statement concerning the dues payable to the association may not be out of place.

By-law 3 of the constitution and by-laws adopted at the 1916 meeting[1] states that "Only such colleges, experiment stations, bureaus, boards or other institutions whose members are active members of this association shall be entitled to enter motions and vote". By-law 10 says: "Each college, experiment station, bureau, board or other institution entitled to representation in the association shall contribute annually $5.00 prior to the first of January following the regular annual meeting". It would appear to follow from this by-law that only those units which have paid the required dues can claim the right to the active participation in the affairs of the association mentioned in By-law 3. This view is supported by the fact that By-law 7 of the old by-laws[2] states that the representatives of the various units entitled to representation shall not be qualified to vote or hold office in the association unless such annual dues have been paid. The purpose of the dues is mainly to provide funds for various expenses in connection with the meetings of the association, such as the printing of programs, etc., and for postage and other expenses incidental to the secretary's work, and

[1] *J. Assoc. Official Agr. Chemists*, 1920, **3**: 586.
[2] *Ibid.*, 1915, 1: iii.

dues are collected only from such units as have sufficient interest in the affairs of the association to pay them.

Nothing is said in the constitution or by-laws about subscriptions to *The Journal*. It appears from the discussion and reports which preceded and attended its establishment[1] that the proposition of increasing the dues to $10 or more for the purpose of financing *The Journal* was discussed. This, however, was not done. It is true that the dues are now $5.00 instead of $2.00 as formerly, but this increase was not made for the purpose of financing *The Journal*, as such an increase in dues would have been entirely inadequate for the purpose. The dues paid to the association have the same significance that they had before *The Journal* was established. If these dues included a subscription, not only would the burden of the association in financing *The Journal* be increased, but the purpose of the dues would in large measure be defeated, since dues then, would not be a direct contribution to the support of the association by those institutional units by which it is controlled, but would assume largely the character of a subscription to the association's journal. Subscriptions to *The Journal* by any of these institutional units or members must be paid for just as if they were individual subscriptions. The subscription rate to institutional as well as to individual members is, however, $4.00, whereas the rate to non-members of the association is $5.00.

In connection with the preparation of the program of the convention for this year the question arose as to the propriety of giving a place on the program to certain attorneys who desired to present matters in which their clients were interested. In this particular instance the matter was probably entirely legitimate, and one in which some of the members of the association are undoubtedly much interested, but as the program was already a full one, the request to present the argument was refused. In this connection attention is called to By-law 9, "Chemists and others interested in the objects of the association may attend its meetings, take part in its discussions, and present papers, if permission is secured from the Executive Committee". The Executive Committee at its meeting Monday night expressed the opinion that the programs should be restricted to members and associate members of the association so far as possible, but that the fullest discussion of subjects presented should be invited and encouraged.

The Executive Committee at its recent meeting considered it necessary to present to the association a by-law definitely providing for the selection of the Board of Editors, as follows:

A Board of Editors of *The Journal* of the association, consisting of five members, one of whom shall be designated the chairman, shall be appointed by the president

[1] *J. Assoc. Official Agr. Chemists*, 1915, 1: 523, 531.

upon recommendation of the Executive Committee. These five members shall serve one, two, three, four and five years, respectively, and each following appointment shall be for five years.

The committee approved of a joint publication with the American Public Health Association on "Standard Methods of Milk Analysis". The matter was referred, with power to act, to R. E. Doolittle, Chairman of the Committee on Revision of Methods, and R. W. Balcom, Chairman of the Board of Editors.

The customary financial statement covering receipts of dues and disbursements from that fund will be found following a similar statement covering receipts and disbursements in connection with the association's publications, submitted by the chairman of the Board of Editors. (See page 248.)

Approved.

G. S. Fraps: It might be well to raise the total sum so it would include the subscription to *The Journal* and then both of these sums could be paid in one transaction.

R. W. Balcom: One reason for not increasing the dues is the fact that they are now fixed by the by-laws, but it might be well to mail the two bills, one for the dues and one for the subscription to *The Journal* at the same time. The dues can not be increased without changing the by-laws.

W. W. Skinner: I do not believe it would be advisable to increase the dues for the purpose suggested for several reasons. I think it was brought out yesterday that the association is supported, as it was always the intention it should be supported, by institutions and not by individuals, but the subscription to *The Journal* is almost entirely individual. As only 15 per cent of the subscription list of *The Journal* represents the individual members of the association, it seems to me that every member should attempt to increase the subscriptions. Otherwise, *The Journal* will be in serious difficulty. Really the support of *The Journal* now comes from libraries, private institutions, commercial concerns and others interested in the proceedings of this association. Only 15 per cent of our own membership believes it sufficiently worth while to subscribe for *The Journal.*

R. W. Balcom: It is less than 15 per cent, I think it is nearer 10, in fact it is less than our foreign subscription list. Our domestic subscriptions have fallen off. The point I wish to make is that if individual members connected with institutions in our various States realized our need we should receive additional subscriptions from the various States that would jump the subscription list up at once to over one thousand. This number would just about finance *The Journal.*

H. D. Haskins: It seems unfortunate that this could not be brought up when we had a larger number of people here to consider this matter. The fact that it has been brought up when there is such a small attendance leads me to suggest that a letter be sent to individual members, which will state the plain facts that have been presented here.

R. W. Balcom: That matter was very carefully considered in the conference of the Board of Editors, and it seemed best, as Dr. Haskins has suggested, to send a letter to the people of our various states, presenting the facts to them and asking for their earnest cooperation in doing what they legitimately can to solicit subscriptions. It would also give us evidence of the interest of the individual members of the association in the association's journal. It is not sufficient for members to place subscriptions for the libraries and to be sure that *The Journal* is there; we need the support of the individual by a four-dollar subscription, and most of us can afford it.

I. K. Phelps: I should like to inquire concerning the income from the *Book of Methods*.

R. W. Balcom: Last year, as I stated, our supply of the first 3,000 copies of the *Book of Methods* was practically exhausted. We informed you that we found it necessary to order 1000 additional copies. The printer ran off 1,224. During the past year we have sold over 600 copies at $5.00, in most cases. We make a 20 per cent reduction to book dealers. We have paid for the 1,224 copies, so that the net profits during the past year have been something like $1500. This year we have on hand approximately 600 copies and if we have as good luck as last year we will dispose of them during the next year and our profits will be practically net. We are depending on that to reduce our deficit. We want to make our *Journal* self supporting so that on future editions of the *Book of Methods* we may be able to reduce the cost.

President Veitch: What is the deficit, Dr. Balcom?

R. W. Balcom: Last year we reported approximately $950. That has been increased. We have not held our own, owing, largely, to the bill for legal services. The deficit is probably in the neighborhood of $1600. If we can sell 600 copies of the *Book of Methods* during the next year or get 100 or 150 individual subscriptions, we can practically wipe out our deficit.

REPORT OF COMMITTEE TO COOPERATE WITH OTHER COMMITTEES ON FOOD DEFINITIONS.

Your committee respectfully submits the following report of the proceedings of the Joint Committee on Food Definitions and Standards for the period since the 1921 meeting of this association.

During the past year the following change in the membership of the committee has occurred: In November, 1921, by reason of a rearrangement in the Bureau of Chemistry affecting the Office of Food Control, F. C. Blanck, appointed in charge of this division, was designated to represent the Department of Agriculture on this committee, *vice* I. K. Phelps.

Another change, which comes closely home to this association, was in consequence of the lamentable death, on January 7th of this year, of Dr. William Frear, chairman of the committee. Reorganization was effected through the selection of W. W. Skinner, Assistant Chief of the Bureau of Chemistry, as chairman, and of E. M. Bailey, chemist in charge, State Agricultural Experiment Station, New Haven, Conn., to represent this association.

For many years Dr. Frear was your senior representative on this committee, and his work and achievements in this connection are well known to you. Although his associates knew that he had been in ill health for a long period, his death, occurring as it did but a few hours following his call convening a special meeting of the committee for the following week, came as a surprise and was received with deep sorrow.

The following resolutions were adopted by his associates on the committee:

Whereas, The sudden death of its chairman, William Frear, in the midst of a most useful life, deprives this committee of the services of its most experienced and capable member, and

Whereas, This committee shares with every association in America devoted to science, to agriculture, to improvement in the quality of food products, and to the enactment and enforcement of pure food legislation, a deep sense of the loss which has befallen us in the death of so distinguished a leader; therefore, be it

Resolved, That this committee extends to the members of the family of William Frear its profound sympathy at this time of their bereavement, and desires to record its affectionate esteem of his sterling honesty, his profound knowledge, his administrative ability and his kindliness of heart; and be it further

Resolved, That, in common with the many scientific organizations of which William Frear was a member or to which his was a familiar name, this committee laments the loss of one whose intellectual clarity, fine sense of justice and breadth of sympathy made him a unique figure among his associates and acquaintances; and be it also

Resolved, That these resolutions be spread upon the minutes of this committee, and that a copy thereof be sent to his family, one to the Secretary of Agriculture of the United States, and one to the Secretary of Agriculture of the State of Pennsylvania.

During the past year three meetings of the committee were held in Washington, in January, June and September. Hearings were given in January to the Association of Cocoa and Chocolate Manufacturers and to representatives of the baking interests. Much of the January meeting was devoted to consideration of a schedule of bread definitions and standards as developed by one of your representatives on the committee. This schedule has been published and, as a result of criticisms and suggestions thereafter received, the standards have been modified in certain minor details and as now presented represent the best judgment of the committee.

In connection with the evaporated milk schedule hearings were given in June to the interests concerned. Following extended hearings upon, and consideration of, the subject of ginger ale, the committee was convinced as to the need of revision of the original definitions and such revision has been effected.

At the September meeting representatives of the spice trade appeared to protest concerning the present ash limits for capsicum and cumin seed and to ask for particular consideration of the specifications for American sage. Affirmative action was taken by the committee as to capsicum, the other topics being reserved for further study. Affirmative action was taken concerning the cinnamic aldehyde content of oil of cassia, and also concerning the revision of definitions and standards for cacao products, butter and renovated butter.

Other subjects still under consideration include macaroni, sirups, mustard, fruit pies, sausage, jams and jellies, almond paste, soy bean flour, fruit juices, ice cream and certain tomato products. The present flour schedule is also due for early revision.

An important change in the policy of the committee, as adopted at the June meeting, involves the prompt publication of all affirmative action. The object of this procedure is to bring the schedules adopted to the attention of all concerned as soon as possible, and thus enable the committee to avail itself of whatever criticisms may be offered before the definitions and standards are presented in final form.

Following full publication to food control officials and to the trade interests concerned, the Joint Committee has finally adopted the following schedule of definitions and standards:

CONDENSED MILK, EVAPORATED MILK, CONCENTRATED MILK.

Definitions and Standards adopted by the Joint Committee on Definitions and Standards, June 22, 1922.

Condensed milk, evaporated milk, concentrated milk, is the product resulting from the evaporation of a considerable portion of the water from milk, or from milk with adjustment, if necessary, of the ratio of fat to non-fat solids by the addition or by the abstraction of cream. It contains, all tolerances being allowed for, not less than seven and

eight-tenths per cent (7.8%) of milk fat, nor less than twenty-five and five-tenths per cent (25.5%) of total milk solids: provided, however, that the sum of the percentages of milk fat and total milk solids be not less than thirty-three and seven-tenths (33.7).

BUTTER.

Butter is the clean, sound product made by gathering in any manner the fat of fresh or ripened milk or cream into a mass, which also includes a small portion of the other natural milk constituents, with or without salt, and contains, all tolerances provided for, less than sixteen per cent (16.0%) of water, and not less than eighty per cent (80.0%) of milk fat. By acts of Congress, approved August 2, 1886, and May 9, 1902, butter may also contain added coloring matter.

RENOVATED BUTTER.

Renovated butter, process butter, is the clean, sound product made in semblance of butter, from melted, clarified or refined butter-fat, without the addition or use of any substance other than water, milk, cream, or salt, and contains, all tolerances provided for, less than sixteen per cent (16.0%) of water, and not less than eighty per cent (80.0%) of milk fat.

GINGER ALE FLAVOR.

Ginger ale flavor, ginger ale concentrate, is the flavoring product in which ginger is the essential constituent, with or without other aromatic and pungent ingredients, citrus oils, and fruit juices.

GINGER ALE.

Ginger ale is the carbonated beverage prepared from Ginger Ale Flavor, sugar (sucrose) sirup, harmless organic acid, potable water and caramel color.

CACAO PRODUCTS.

Definitions and standards adopted by the Joint Committee on Definitions and Standards, September 29, 1922.

1. *Cacao beans, cocoa beans,* are the seeds of trees belonging to the *genus Theobroma,* especially those of *Theobroma cacao* L., and closely related species.

2. *Cacao nibs, cocoa nibs, "cracked cocoa",* are roasted or dried cacao beans, broken and freed from germs and from shell or husk.

3. *Chocolate, plain chocolate, bitter chocolate, chocolate liquor, chocolate paste, bitter chocolate coating*[1], is the solid or plastic mass obtained by grinding cacao nibs and contains not less than fifty per cent (50%) of cacao fat and, on the moisture and fat-free basis, not more than eight per cent (8%) of total ash, not more than four-tenths per cent (0.4%) of ash insoluble in hydrochloric acid and not more than seven per cent (7%) of crude fiber.

4. *Sweet chocolate, sweet chocolate coating,* is chocolate mixed with sugar (sucrose), with or without the addition of cacao butter, spices, or other flavoring materials, and contains, on the moisture-, sugar- and fat-free basis, no greater percentage of total ash, ash insoluble in hydrochloric acid, or crude fiber, respectively, than is found in moisture- and fat-free chocolate.

5. *Milk chocolate, sweet milk chocolate,* is the product obtained by grinding chocolate with sugar, with the solids of whole milk, or the constituents of milk solids in pro-

[1] Definitions and standards for alkalized products will form a separate schedule.

portions normal for whole milk, and with or without cacao butter and/or flavoring material. It contains not less than twelve per cent (12%) of milk solids.

6. *Cocoa, powdered cocoa,* is chocolate deprived of a portion of its fat and pulverized, and contains, on the moisture- and fat-free basis, no greater percentage of total ash, ash insoluble in hydrochloric acid, or crude fiber, respectively, than is found in moisture- and fat-free chocolate.

7. "*Breakfast cocoa*" is cocoa which contains not less than twenty-two per cent (22%) of cacao fat.

8. *Sweet cocoa, sweetened cocoa,* is cocoa mixed with sugar (sucrose), and contains not more than sixty-five per cent (65%) of sugar in the finished product, and, on the moisture-, sugar- and fat-free basis, no greater percentage of total ash, ash insoluble in hydrochloric acid, or crude fiber, respectively, than is found in moisture- and fat-free chocolate.

9. *Sweet milk cocoa* is the product obtained by grinding cocoa with sugar, with the solids of whole milk, or the constituents of milk solids in proportions normal for whole milk, and with or without flavoring material. It contains not less than twelve per cent (12%) of milk solids.

C. EDIBLE VEGETABLE OILS AND FATS[1].

Cacao butter, cocoa butter, is the edible fat obtained from sound cacao beans (seeds of *Theobroma cacao* L., or other closely related species), either before or after roasting.

BREADS.

Bread is the sound product made by baking a dough consisting of a leavened or unleavened mixture of ground grain and/or other clean, sound, edible farinaceous substance, with potable water, and with or without the addition of other edible substances.

In the United States the name "bread", unqualified, is understood to mean wheat bread, white bread.

Wheat bread dough, white bread dough, is the dough consisting of a leavened and kneaded mixture of flour, potable water, edible fat or oil, sugar and/or other fermentable carbohydrate substance, salt and yeast, with or without the addition of milk or a milk product, of diastatic and/or proteolytic ferments, and of such limited amounts of unobjectionable salts as serve solely as yeast nutrients[2], and with or without the replacement of not more than three per cent (3%) of the flour ingredient by some other edible farinaceous substance.

Wheat bread, white bread, is the bread obtained by baking Wheat Bread Dough in the form of a loaf or of rolls or other units smaller than a loaf. It contains, one hour or more after baking, not more than thirty-eight per cent (38%) of moisture, as determined upon the entire loaf or other unit.

Milk bread is the bread obtained by baking a wheat bread dough in which not less than one-third (⅓) of the water ingredient has been replaced by milk or the constituents of milk solids in proportions normal for whole milk. It conforms to the moisture limitations for Wheat Bread.

Rye bread is the bread obtained by making a dough which differs from Wheat Bread Dough in that not less than one-third (⅓) of the flour ingredient has been replaced by rye flour. It conforms to the moisture limitation for Wheat Bread.

---

[1] U. S. Dept. Agr. Circular 136, 17.
[2] NOTE—The propriety of the use of minute amounts of oxidizing agents as enzyme activators is reserved for future consideration and without prejudice.

Raisin bread is the bread obtained by baking Wheat Bread Dough, to which have been added sound raisins in quantity equivalent to at least three (3) ounces for each pound of the baked product and which may contain proportions of sweetening and shortening ingredients greater than those commonly used in Wheat Bread Dough.

Brown bread, Boston brown bread, is a bread made from rye and corn meals, with or without flour, whole-wheat flour, and/or rye flour, with molasses, and in which chemical leavening agents, with or without sour milk, are commonly used instead of yeast.

In some localities the name Brown Bread is used to designate a bread obtained by baking a dough which differs from Wheat Bread Dough in that a portion of the flour ingredient has been replaced by whole-wheat flour.

D. CONDIMENTS (OTHER THAN VINEGAR AND SALT)[1].

Definitions and standards adopted by the Joint Committee on Definitions and Standards, September 29, 1922.

b. FLAVORING EXTRACTS[2].

5a. *Oil of cassia* is the lead-free volatile oil obtained from the leaves or bark of *Cinnamomum cassia* Bl., and contains not less than eighty per cent (80%) by volume of cinnamic aldehyde.

a. SPICES.

10. *Cayenne pepper, cayenne*, is the dried, ripe fruit of *Capsicum frutescens* L., *Capsicum baccatum* L., or some other small-fruited species of Capsicum. It contains not less than fifteen per cent (15%) of nonvolatile ether extract, not more than one and five-tenths per cent (1.5%) of starch, not more than twenty-eight per cent (28%) of crude fiber, not more than eight per cent (8%) of total ash, nor more than one and twenty-five hundredths per cent (1.25%) of ash insoluble in hydrochloric acid.

Respectfully submitted,

JULIUS HORTVET, C. D. HOWARD,
E. M. BAILEY.

Committee to Cooperate with Other Committees on Food Definitions.

Approved.

Following the report of the Committee to Cooperate with Other Committees on Food Definitions, E. M. Bailey also read the following communication, which had been sent to the secretary September 16, 1922:

GENTLEMEN:

The three members of your association who are your representatives upon the Joint Committee on Definitions and Standards, desire to call your attention to a difficulty which has in the past seriously hampered their work and to request of you such formal action as will relieve the situation.

At each of the annual conventions of this association it has been the custom to have the chairman of the group of your representatives upon the Joint Committee report to the association the definitions and standards which that committee has formulated since the last convention. By vote of the convention these definitions and standards

[1] U. S. Dept. Agr. Circ. 136, 11.
[2] *Ibid.*, 15.

have then been approved, and, after similar approval by the Dairy, Food and Drug Officials, they have been submitted to the Secretary of Agriculture for consideration and for such action as he may see fit to take in the premises. No definitions or standards have been submitted to the secretary except after formal approval by the two associations.

Until recently, the committee has taken the stand that, after agreement had been reached upon the formulation of any item, it was incumbent upon the members to refrain from giving out any information concerning such action until the matter had been formally presented to one or other of the associations for its approval. Applications made during the interval for information with regard to the action taken, were therefore met with refusal, explanation being given that the decisions were only tentative until approval by the association had been secured.

At a recent meeting, the committee considered this matter anew and decided that such a rule was disadvantageous to all concerned. It was bound to result in the presentation to that association, whose annual meeting came first, of matters of which the members of such association had no previous knowledge, and in calling upon them to approve or to disapprove of action into the reasonableness of which they had had no opportunity to examine. As a result, the vote of the association was of necessity perfunctory, and its value practically negligible. In the same way the trade, having no knowledge of the action of the committee prior to the annual convention of the association, were stopped from bringing criticism to bear at the very time when such criticism should be heard.

Accordingly, the committee decided to publish its decisions as soon as possible after its sessions, and thus to show its desire that its action receive prompt consideration and be subjected to proper criticism. Under the procedure hereinafter proposed, should valid objection from any source be made to the definition or standard formulated, there would be opportunity for the committee to withhold its recommendation and to reconsider the matter before its presentation to the secretary.

Since the meetings of the associations take place but once a year, while those of the Joint Committee are held three or four times in each year, it follows that the decisions of the committee must, under the present arrangement, lie in abeyance anywhere up to a year before they can be recommended to the secretary. This delay is frequently a source of great annoyance to administrative officials and to the trade. If there were, in our opinion, any compensating advantage gained through this method of handling the matter, we should hesitate to bring the question before you; but, so far as we have been able to observe, the associations have in each case felt that they were not in a position to pass judgment upon the work of the committee and hence have given their formal approval practically without discussion of any kind.

In order, therefore, to eliminate this delay, we request that you grant to your representatives upon the Joint Committee on Definitions and Standards the authority, for you and in your name, to approve such definitions and standards as, after careful consideration, they believe to have been couched in satisfactory form.

In conclusion, let it be said with all emphasis, that your representatives upon the Joint Committee do not, in asking the association to grant them this power to act, desire to arrogate to themselves an authority which should not be theirs. Their aim is simply to remove an impediment which is a cause for delay and therefore a source of annoyance and which serves no useful purpose so far as they can see. They know, and they believe the association recognizes, that they have given the matters upon which they have come to a decision prolonged consideration; have secured a mass of information from all available sources known to them; have consulted with representatives of the trade in public conferences; and have used their best ingenuity to put their conclusions into clear, terse wording. They do not believe—and the history

of this question seems to bear them out in this—that hasty consideration, at a busy convention, of the definitions and standards proposed, is likely to result in any good at all comparable with that secured through the speedy reference of the matter to the consideration of the Secretary of Agriculture and his advisers.

We are

Very respectfully,
JULIUS HORTVET,
C. D. HOWARD,
E. M. BAILEY.

It was moved, seconded and carried that the power of approval requested be granted to the Committee to Cooperate with Other Committees on Food Definitions.

W. W. Skinner: The following letter, dated Nov. 13, 1922, relating to the subject of evaporated milk was received from the Van Camp Packing Co.:

Mr. W. W. SKINNER, *Secy-Treas.*,
Bureau of Chemistry,
Association of Official Agricultural Chemists,
Washington, D. C.

DEAR SIR:

Due to the fact that the question of the proposed change in the existing regulation governing the manufacture of Evaporated Milk is to be brought before the meeting of the Association of Official Agricultural Chemists at Washington, D. C. for its consideration, we desire to register our continued protest against any change being made in the existing regulation which would tolerate manipulation in modifying the fat and solids of the whole milk which enters into the manufacture of Evaporated Milk, thereby nullifying the existing regulations which require that Evaporated Milk shall be manufactured from whole milk only.

We are enclosing copy of written argument which we submitted to the Joint Committee on Definitions and Standards in Washington, D. C., June 19, 1922 in protest against any change in the existing regulation, and request that this letter and our protest be read before the open meeting; also referred to the committee having this matter in charge.

Yours very truly,
The Van Camp Packing Company, Inc.
(Signed) C. W. Mann,
Vice President.

The secretary brought this letter to the attention of the Executive Committee Monday night, the matter was carefully considered and it was decided that it should be read before the general meeting, but that the argument which had been previously considered by the Standards Committee should not be read unless it was demanded by some member of the association. The Executive Committee believed that the open meeting was no place to present such an *ex parte* statement.

President Veitch: The question is on the adoption of the report of the Committee to Cooperate with Other Committees on Food Definitions.

H. C. Lythgoe: I wrote a letter to the secretary of the association shortly after these new proposed changes were submitted. The objection I have is that the definition for evaporated milk is apparently in conflict with the law. The law regards as adulterated any article of food from which anything has been taken away. The various laws of the different States and the standards of this association recognize milk as whole milk from which no cream has been removed and to which no water has been added. The statutes of many States require the law-enforcing body to adopt the standards of this association, or rather the standards of the Secretary of Agriculture, whenever those standards do not conflict with the law. The adoption of these standards by such law-enforcing bodies comes under the same provision of law as the making of regulations. All such regulations must, in the first place, be reasonable and, in the second place, must conform with the law in order to be effective. I question very seriously whether this change could be legally adopted by any of the States having such statutes as I have quoted. In the State of Massachusetts I am sure we could not. We shall not have this problem, because we have a special statute covering the sale of condensed milk and under that statute all condensed milk that has not all the cream in it must be labelled condensed skim milk. I had a talk with the Chairman of the Standards Committee and we decided the question was merely an academic one. I am convinced that not only condensed milk but uncondensed milk is greatly manipulated. If we can get the evidence of such manipulation, the seller of such milk can be prosecuted. I see no reason why a special name could not be devised which would recognize that practice and legalize it.

President Veitch: The whole argument from all points of view has been considered by the Standards Committee. Now, do we, in view of all these facts and in view of the fact that we won't get the information and have not the time to do it if we could get the information, want to get into this thing at this time? I think there is nothing to do but leave it to the Standards Committee.

W. W. Skinner: May I say a word? Naturally I would hesitate to be drawn into an argument or controversy with my good friend from Massachusetts or any other member of the association about the work of the Joint Committee on Definitions and Standards and I hesitate somewhat to attempt an explanation, although I believe it is due. The reason the Executive Committee did not attempt to review this matter is that it can not possibly consider questions of this kind intelligently unless it is going to devote a large amount of time to them. Let me say to you that this milk situation has been discussed for many years by those in the industry and officials interested in evaporated milk. The Bureau of Chemistry alone, I think, has given it consideration for

some ten or twelve years, and for more than two years, in cooperation with the Milk Committee of the National Canners Association and the Committee of the Milk Producers' Association, has conducted elaborate experiments. So a great mass of information has accumulated and is available to the Standards Committee. It would take any one of you more than a week to digest the accumulated data which have been collated and critically reviewed by the Standards Committee over a period of several sessions. I do not care to carry this argument very far at this time because, as Mr. Lythgoe has said, it is somewhat of an academic question. We could argue indefinitely about these things. At times the members of this association and others may overlook the philosophy which must govern the deliberations of the Standards Committee and fail to appreciate the significance of the title Joint Committee on Definitions and Standards. The question generally is in regard to definitions. Now, as I have stated before, we have to define things, not necessarily as they are in the literal sense but as they exist under present conditions, and we have no authority or right to set up ideals and attempt to translate them into either definitions or standards. So, I would say to my friend, Dr. Huston, in regard to the amount of raisins in raisin bread, or currants in currant bread—which he questioned after hearing the definition—that we have investigated the matter thoroughly and have interviewed the people who could give us information. We have learned what the industry means by raisin bread and what the public thinks is the best raisin bread and upon the evidence we have determined the limit of the quantity of raisins in a product called raisin bread. The Committee on Definitions and Standards must sit in judgment as a court basing its judgment upon the evidence. The evidence in this case shows that 3 ounces per pound is about the lowest limit of raisins a product should contain which is called, and made and sold as, raisin bread. You may say, "I do not want that, I want a 50 per cent raisin bread". Someone else would call 50 per cent raisin bread a fruit cake. I merely use raisin bread as an illustration. We are trying to define the bread which has been known and sold by the best bakers as raisin bread, and if you get a pound loaf with 3 ounces of raisins in it, the committee is ready to say that you are getting about all you are entitled to. At the bakers' convention in Chicago, I was taken to task for our definition of rye bread. In the investigations made we found that a small amount of rye bread baked for certain of our foreign population is made, as a rule, of all-rye flour, but that generally no all-rye-flour bread is sold to the American people and marketed under that name. A limited quantity of so-called rye bread is also made by certain bakers for the Jews who like less than 20 per cent of rye. These bakers say, "What are we going to do?" The committee had to draw the line somewhere and so concluded from the best evidence that the limit should be 33 per cent

rye flour for American rye bread, a standard which would conform to the best baking practice.

I am only telling you these things to show you what the philosophy of the committee has to do with the making of definitions and standards. The proposed standard for evaporated milk is higher than the present standard; under it either the solids or fat, or both, must be increased. The old standard was based upon the data for sweetened condensed milk; this was unwise since such data are not always applicable. The present standard has been complied with by modifying the milk—adjusting it to meet the numerical limits prescribed. Mr. Lythgoe knows, and I am sure he will verify this, that most of the milk sold in Boston and other cities is made to comply with the numerical standards by adjustment. The milk may be adjusted by the farmer, by the distributor, and by the factory.

The question seems to be: "What is evaporated milk and what ought evaporated milk to be when you buy it?" Certainly you would not regard as an undesirable practice the addition of cream to a milk too poor in cream to make a satisfactory evaporated product; that has been the attitude of the committee. On the other hand, in a certain section of the country, it is alleged, the end of the lactation period of the cows occurs at about the same time for the entire herd; under these conditions the milk is so high in fat in relation to the solids that it can not be evaporated successfully without causing trouble from granulation. Adjustment of this milk is of no detriment to the consumer under the proposed standard. He will get a higher product than he has in the past, and the product of the herds may be used for the entire lactation period. The committee believes that this proposed standard for evaporated milk is a fair and just one.

H. D. Haskins: Your Committee on Definitions of Terms and Interpretation of Results on Fertilizers held a meeting and considered the questions which had been proposed by control officials and by commercial and trade chemists and we propose to make a short, formal report at this time. In making definitions and interpreting results, I think this committee should go slow in what it officially recommends for adoption by the association. It was rather a question as to how this committee could best function. We finally decided that it would be wise to follow the procedure of the Association of Feed Control Officials—that is, to allow a free and full discussion on any subject that may be proposed, in an open meeting of the committee, and prior to this meeting to furnish a list of subjects to the control fertilizer chemists, the trade chemists and the commercial chemists. Then, after a full and free discussion, allow the committee to go into session and formulate its definitions and interpretations of results and bring them before the association, as provided in the amendments to the by-laws that were pro-

posed this morning. It will be understood that there will be no discussion at this time on the subjects which will be mentioned in the formal report, but that there will be opportunity for free and full discussion by everybody interested a year hence; provisions will be made for that in a suitable place, probably prior to the next meeting of the association. I shall now read the formal report which this committee wishes to make to the association this morning.

REPORT OF THE COMMITTEE ON DEFINITIONS OF TERMS AND INTERPRETATION OF RESULTS ON FERTILIZERS.

The committee, after organization, considered a list of questions which had been submitted for its deliberations. It was the unanimous opinion of the committee that full and free discussion should be allowed on any appropriate subject, and it was therefore voted that suggested questions should be considered for a term of one year, then to be discussed in the presence of the committee by any one interested, prior to any recommendations as tentative definitions and rulings. The following subjects for definition and ruling are therefore submitted for consideration and study:

1. BASIC PHOSPHATIC SLAG.

Basic phosphatic slag is a by-product in the manufacture of steel from phosphorus-containing iron ores. The product shall be finely ground and shall contain no admixture of materials other than what results in the original process of manufacture. It shall contain not less than 12% of total phosphoric acid, and not less than 80% of the total phosphoric acid shall be soluble in 2% citric acid solution according to the Wagner method of analysis. Any phosphatic slag not conforming to this definition shall be designated as low grade.

2. INTERPRETATION OF THE WORD "LIME" AS APPLIED TO FERTILIZERS.

The term "lime" shall not be used in the registration, labelling, or guaranteeing of fertilizers or fertilizing materials, unless the "lime" is in a form to neutralize soil acidity, such as the oxide, hydroxide, or carbonate, or equivalent magnesia compounds.

3. DRIED PULVERIZED OR SHREDDED MANURES.

Dried pulverized or shredded manures shall be only what the name indicates, and not mixtures of pulverized manures and other materials.

Definitions for the following proposed subjects have not yet been formulated:

Unleached wood ashes.
Leached wood ashes.
Ashes from leached wood.
Double manure salts.
Manure salts.
Dissolved bone and potash.

Additional questions which have been considered:

(1) *Shall the committee encourage and urge the practice of including the formula grade of fertilizer with the brand name?*

The committee recommends and urges the practice of including the formula grade of fertilizer with the brand name, depending upon the section of country where the product is sold; for example, grade 4-8-4 or 8-4-4.

(2) *The question of a uniform plan of reporting fertilizer analysis in control work. What should constitute a proper detailed analysis report?*

The committee would encourage not only a study of the quantity of plant food guaranteed in any fertilizer, but also a study by any methods that might result in the improvement of the quality of said plant food, even though this was not called for in the fertilizer law.

(3) *Interpretation of results on nitrogen availability.* The committee does not feel prepared at this time to offer any suggestions on this subject.

Proposed subjects which the committee feels could be more appropriately handled by the fertilizer referee and so recommends:

(1) The consideration of grinding analytical fertilizer samples finer than through a 1 mm. round-hole sieve.

(2) A suggestion that the official method for the determination of ammonia in fertilizers be interpreted as being applicable to sulfate of ammonia, and that further study be made on the determination of moisture in this salt.

(3) A further investigation of the determination of total and insoluble phosphoric acid in vegetable meals and in mixtures containing them.

The committee welcomes suggestions and further subjects by any one interested.

H. D. Haskins, E. G. Proulx,
R. N. Brackett, J. W. Kellogg,
G. S. Fraps.
Committee on Definition of Terms and Interpretation of Results on Fertilizers.

Approved.

REPORT OF AUDITING COMMITTEE.

The Auditing Committee has had submitted to it the financial report on publications of R. W. Balcom, Chairman, Board of Editors, covering the period from October 15, 1921, to October 31, 1922. The report was found to be in good order, with proper and sufficient vouchers for all disbursements.

The committee has also examined the report of W. W. Skinner, Secretary-Treasurer, covering the same period, and has found the account to be correct, with proper vouchers for all disbursements.

Respectfully submitted,
C. M. Bradbury,
J. B. Reed.
Auditing Committee.

Approved.

R. N. Brackett: When the general referees were first appointed, I understood that the appointment was intended primarily to enable us to have some one in authority to take up any new work that might arise between the annual meetings of the association. The question of general referees arose at the time of the borax trouble. If there had been a general referee he might have taken up the subject and appointed appropriate referees. I took the liberty last year of adding an extra referee on potash, but as some members of the association considered that by this action I was overstepping my authority, Dr. Skinner thought it would be well to decide whether the general referee had any authority to appoint another referee on a subject.

J. W. Kellogg: If it is in order, I will make a motion to the effect that it is the sense of the association that the general referee has the authority to appoint associate referees as the occasion arises.

P. F. Trowbridge: I take exception to that. We should encourage the work but it seems to me that the referee should wait another year, or report any extra work under his name. I do not believe that any individual member of the association ought to assume the responsibility of naming an associate referee. I think it does not need any action.

B. B. Ross: It was my understanding that the point was made that the general referee, in investigating work before the association meeting, would have the authority either on his own initiative or through the Executive Committee to secure an associate referee.

President Veitch: Yes, on points not covered by a referee.

B. B. Ross: If it is understood that he has that authority, that is all right.

P. F. Trowbridge: It ought to come to the Executive Committee.

President Veitch: It is the sense of the meeting, if I may voice it, that when an additional associate referee is needed in the interim, referees should be designated by the Executive Committee on the recommendation of the general referee.

B. B. Ross: This is unofficial business which some of us have discussed informally on the outside. It has been suggested that inasmuch as we attend here in a very large group and have no opportunity to get together in a social way at any time it would be well to set apart one night for a smoker or Dutch lunch for the members and chemists attending the meeting. We could get together in an informal social way, become better acquainted and do some reminiscing. I move that this step be taken and that in the notice of the meetings to be sent out in advance mention be made of the fact that some evening, say the second evening of the convention, be set apart for such a social gathering.

It was moved, seconded, and carried that the second evening of the association's convention be set apart for an informal social meeting.

REPORT OF NOMINATING COMMITTEE.

Your committee respectfully submits the following names:

President: A. J. Patten.

Vice-President: R. E. Doolittle.

Secretary-Treasurer: W. W. Skinner.

Additional Members of the Executive Committee: E. M. Bailey and P. B. Dunbar.

R. W. BALCOM, J. W. KELLOGG.
J. B. WEEMS,
Nominating Committee.

It was moved, seconded and carried that the secretary be directed to cast a unanimous ballot for the officers nominated.

REPORT OF COMMITTEE ON RESOLUTIONS.

Since the last meeting, the association has lost by death one of its oldest and most valued members.

Dr. William Frear, Professor of Agricultural Chemistry in Pennsylvania State College, and Vice-director of the Agricultural Experiment Station, died suddenly of apoplexy at his home at State College, on January 7, 1922.

As a member of the Association of Official Agricultural Chemists for nearly thirty-five years, Dr. Frear rendered notable and conspicuous service as referee, as a member of the Executive Committee, chairman of the Committee on Abstracts, chairman of the Committee on Food Standards, member of the Board of Editors of *The Journal*, member of numerous special committees, and as president of the association. He had also served as editor of *Agricultural Science* and as president of the Society for the Promotion of Agricultural Science, while as chemist in charge of fertilizer control work and as chemist for several State boards in Pennsylvania he contributed in a notable way to the development and progress of scientific agriculture in his own State and in the Nation.

Your committee recommends the adoption of the following resolution:

Resolved, That in the death of Dr. William Frear this association has lost a member who, throughout a large part of the life of the association, was a conspicuous factor in promoting the progress and success of this organization, giving unstintedly of his time, his talents and his energy to the furtherance of its work along many of its lines of service. As an officer and member of the association, he was at all times earnest, diligent and faithful in the performance of the tasks allotted to him,

leaving behind him a record of conspicuous fidelity and efficiency in the discharge of duty. As a friend and colleague, he was sincere, loyal and true, while in his uprightness of life and character he was worthy of the emulation of all who knew him.

Resolved, That the secretary of the association be instructed to send a copy of this resolution to the family of our deceased colleague.

Resolved, That this association expresses to the Honorable Henry C. Wallace, Secretary of Agriculture, its thanks for his valuable and inspiring address.

Resolved, That this association appreciates the impartial, skilful and courteous manner in which the president, F. P. Veitch, has discharged the duties of his office.

Resolved, That this association is indebted to the Chairman of the Board of Editors, R. W. Balcom, for the excellent preparations made for this convention and for the efficient manner in which the affairs of *The Journal* have been conducted.

Resolved, That the association desires to express its commendation of the efficient work of the secretary and his various assistants for their untiring efforts in making this meeting a success.

Resolved, That the thanks of this association are due the management of the Raleigh Hotel for the use of the various rooms and other courtesies extended to it and its members.

Resolved, That this association go on record as heartily endorsing the campaign recently inaugurated by the American Chemical Society to educate the American people to a better understanding of chemistry, its possibilities and its applications to every-day life.

B. B. Ross, H. B. McDonnell.
G. L. Bidwell,
Committee on Resolutions.

Approved.

FIRST DAY.

WEDNESDAY—MORNING SESSION.

REPORT ON WATER.

By J. W. SALE[1] (Bureau of Chemistry, Washington, D. C.), *Referee.*

Last year it was recommended that the quantitative methods for the determination of lead, copper and zinc[2] be studied during the present year. Four synthetic samples of water were prepared and sent to the cooperating analysts, together with detailed methods of procedure. However, prior to issuance of these samples, preliminary work showed conclusively that it would be necessary to revise the procedure for copper as published[3]. It was found that frequently sufficient iron was occluded with the precipitate of copper sulfide to produce an interfering blue color (Prussian blue) when the reagents were added. The method was usually satisfactory when the sample contained only small amounts of iron, but the procedure was not suitable for general application. The method was modified, therefore, to eliminate residual traces of iron and in the new procedure the evaporation to dryness was avoided. The revised method follows:

COPPER.

(To be substituted for the method for copper[3])

Boil the moderately acid filtrate, which contains iron, copper and zinc, to remove alcohol; adjust solution to a volume of about 200 cc. and add 1 gram of ammonium chloride. Heat to boiling, saturate with hydrogen sulfide gas, boil to remove precipitated sulfur, cover beaker, let stand about 2 hours or until supernatant liquid becomes clear, filter and wash the copper sulfide without intermission with water containing hydrogen sulfide. Collect filtrate in a porcelain casserole. Dissolve the copper sulfide in hot dilute nitric acid (1 to 5). Cool, add a few drops of phenolphthalein, and make the solution slightly alkaline with a 2½% solution of ammonium hydroxide, added carefully from a dropping bottle. Add 10 cc. of a 10% solution of ammonium nitrate, adjust the volume to 100 cc., and boil gently until a test with red litmus paper shows the solution to be neutral. Filter the solution to remove any iron which may be present, and adjust the filtrate to a volume of 100 cc. Add to an aliquot, 3 drops of potassium ferrocyanide solution (c)[3]. Compare color obtained with standards containing 0.1, 0.2, 0.3, 0.4 and 0.5 mg. of copper. Prepare these standards by measuring out the appropriate amounts of standard copper solution; add phenolphthalein, a slight excess of dilute ammonium hydroxide and 1 cc. of a 10% solution of ammonium nitrate, boiling the solution until neutral to red litmus, cooling and adding three drops of potassium ferrocyanide. Make the colorimetric comparison in 100 cc. Nessler jars.

---

[1] Presented by W. W. Skinner.
[2] *J. Assoc. Official Agr. Chemists*, 1922, 5: 382.
[3] *Ibid.*, 383.

This method for copper and the methods for lead and zinc referred to previously, together with the synthetic samples, were sent to the following analysts: 1. W. H. Simms (S. H. Wilson), 2. J. B. Wilson, 3. C. H. Badger, 4. A. E. Mix, 5. W. E. Shaefer, 6. J. W. Sale. The data obtained are given in Table 1.

TABLE 1.

Collaborative results on analysis of synthetic water samples.

(All figures are expressed in milligrams per 10 cc. of sample.)

ANALYST NO.	1	2	3	4	5	6	MAXIMUM	MINIMUM	AVERAGE	PRESENT
Sample 1*										
Lead.......	5.0 5.0	5.0 4.6	4.3 4.4	4.7 4.7	5.0 5.1	4.5 4.5	5.1	4.3	4.8	4.7
	5.0 5.0	4.4 5.0		4.8 4.8	5.1					
Copper.....	5.0 5.0	5.0 5.3	6.0 6.0	5.5 5.5	....	5.0 5.5	6.0	5.0	5.4	5.5
		6.0 5.5		5.5 5.5						
Zinc.......	5.0 5.0	6.0 7.0	5.0 5.0	5.0 5.0	....	4.8 4.6	7.0	4.6	5.3	5.0
	5.0 5.0	6.0 7.0		5.0 5.0						
Sample 2*										
Lead.......	5.0 5.0	5.4 5.0	4.9 5.0	5.3 5.4	5.1 5.4	4.8 5.0	5.5	4.8	5.2	5.5
	5.0 5.0	5.4 5.0		5.5 5.5	5.4					
Zinc.......	5.0 5.0	4.4 4.4	5.1 5.1	5.5 5.5	5.0 5.2	5.2 5.4	5.5	4.0	4.9	5.5
	4.0 5.0	4.0 4.2		5.5 5.5						
Sample 3*										
Lead.......	5.0 5.0	4.8 4.8	4.7 4.7	5.0 5.0	5.1 4.9	4.8 5.0	6.0	4.0	5.0	5.0
	6.0 6.0	4.0 4.4		5.0 5.0	5.4					
Iron.......	....	....	....	....	....	....	....	....	....	....
Color......	....	....	....	....	....	....	....	....	....	....
Sample 4										
Lead.......	6.0 6.0	3.6 3.6	4.5 4.5	4.0 4.2	4.7 4.5	4.5 4.5	6.0	3.6	4.6	4.2
	6.0 6.0	4.0 3.6		4.2 4.2	4.6					

*Sample 1 contained also 4.5 mg. of aluminium, 5.5 mg. of iron, and color; Sample 2, 5.0 mg. of iron; and Sample 3, 1.0 mg. of iron and color. These metals and color were added because of their possible interference with the accuracy of the determination of lead, copper and zinc.

DISCUSSION.

The results are fairly satisfactory when several factors are given consideration. In the first place, Samples 1 and 3 are quite complex solutions, iron and caramel color being decidedly interfering ingredients in the determination of lead, copper and zinc. In the second place, the methods are colorimetric or more especially turbidimetric, and subject to the limitations of these types of methods. When the color of a sample has a slightly different shade from that of the standard, the accuracy of the color comparison is diminished. For example, a difference of 0.005 mg. of lead in the form of lead sulfide in a Nessler tube can easily be detected in a set of standards ranging from 0.01 to about 0.1 mg. of lead, whereas the actual reading error of the samples may be twice this amount or about 0.01 mg., due to the samples possessing a slightly different shade. This reading error is multiplied by 25, 50 or even 100, depending on the aliquot taken, so that there is an unavoidable reading

error ranging from 0.2 to 1.0 mg., although 1.0 mg. is considered unnecessarily high. The referee is of the opinion that the variations from the correct figures in Table 1 are due chiefly to the error in comparing the color and turbidities of the samples and not to the separation of the metals. Then, finally, the inexperience of the analysts with these methods must be considered. Analyst No. 2, for instance, is an organic chemist who never had occasion to determine metals quantitatively. On the other hand, the excellent results obtained by Analyst No. 4 may be attributed to long experience in exact analytical work. It would appear that the acceptability of the methods should be based largely on the results obtained by those who have had experience in this kind of work. In view of all the circumstances, however, the referee will recommend that the methods for lead and zinc and the method for copper be adopted as tentative methods only and not as official methods.

The referee does not recommend any specific procedure to be followed by the Referee on Water for 1923, but suggests that the methods for salt[1] be extended.

RECOMMENDATIONS.

It is recommended—

(1) That the method for lead and zinc be adopted as a tentative method.

(2) That the method for copper, as given in this report, be adopted as a tentative method.

(3) That additional methods for the analysis of salt be studied next year.

REPORT ON TANNING MATERIALS AND LEATHER.

By F. P. Veitch[2] (Bureau of Chemistry, Washington, D. C.), *Referee.*

As has been the case for several years, all cooperative work on tanning materials and leather has been carried on with and in the American Leather Chemists Association. While the detailed reports of the work can be found in the journal of that association, it is believed that it will be of interest to you to summarize briefly the findings and points raised within the last year, in so far as they relate to analytical procedures.

It will be recalled that in the last report reference was made to some data which strongly indicated an influence of relative humidity upon moisture determinations in leather. Further work, both individually and cooperatively, has confirmed this. The collaborator who obtained the lowest moisture result worked under the highest average relative humidity conditions, while the one who operated under the lowest average relative humidity got the highest percentage of moisture. The

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 384.
[2] Presented by R. W. Frey.

differences, however, were too great to be attributed entirely to variations in humidity. Unknown factors of equipment and manipulation of greater disturbing influences were indicated. They were further evidenced by detailed individual work under varied relative humidities which showed that a single operator can obtain closely agreeing results under any given humidity and that under different humidities the variations in percentage of moisture are reasonably within the expected range from the influence of relative humidity.

Since the determination of magnesium is so general it may be of interest to mention the essential points in the report of a committee of the American Leather Chemists Association on the determination of epsom salts in leather. As you know, the presence of excessive quantities of ammonium salts and precipitant gives inaccurate results when precipitating magnesium as ammonium magnesium phosphate. It was shown that the time for double precipitation or the trouble of removing the excess of ammonium salts could be avoided by the simple expedient of using an aliquot of the ash solution equivalent to two grams of leather instead of the original ten-gram charge. This so reduced the concentration of magnesium that single cold precipitation without removal of salts gave as accurate results as did double cold precipitation. It was also shown, regardless of the concentration of magnesium up to that given by the full ten-gram ash charge, that a single hot precipitation as phosphate without previous destruction of excess ammonium salts gave results in very close agreement with those by double cold precipitation.

The estimation of glucose is another item of general interest. Among the difficulties with this determination in leather analysis is one which you have frequently met in food analysis. It has long been recognized in the gravimetric determination of sugar by reduction with Fehling that with impure solutions the presence of inorganic constituents, such as iron and magnesium, will give inaccurate and high results. You will recall several papers given before this association dealing with this feature. In the report of the Referee on Tea and Coffee[1], it was found that in working with coffee the effect of magnesium and iron was so great as to make the gravimetric results for sugar worthless. Of course, in such instances, recourse is had to the volumetric or electrolytic procedures for determining the actual copper thrown down. There remains, however, the objection that if the magnesium, especially, is not previously removed, its precipitation in the Fehling solution does, at times, seriously interfere with the filtration of the cuprous oxide. Aside from this, there is also a rather insistent demand for a gravimetric procedure on more or less of an assumption of greater convenience and time saving. For the past several years committees of the American Leather Chemists

[1] *J. Assoc. Official Agr. Chemists*, 1920, **3**: 498.

Association have been working on this problem without a great deal of success. Attempts to remove the magnesium present from the added epsom salts, as hydroxide and phosphate, have at times looked promising but have not always given consistent results. The results have indicated, however, that sodium phosphate is an excellent deleading agent. Work is being continued on this problem but it begins to look as if the object in mind hardly justifies the immense amount of detailed work it will require.

In the determination of chromium in leather ash it has been shown that fusion with sodium peroxide gives low results in the presence of barium salts unless a second fusion is made. It has been recommended that the peroxide fusion be discarded, and that a fusion mixture of equal parts of sodium carbonate, potassium carbonate and borax glass be retained.

The question of the best solvent for the extraction of oils and greases from leather is still an open one, though much committee work has been done on it. The latest report is in favor of retaining petroleum ether in preference to chloroform. Though previous work has shown the decided superiority of chloroform as an oil and grease solvent, it has also been found that it extracts from leather appreciable quantities of materials other than oils and greases. This extraction depends largely upon the moisture present in the leather, a point which the data of the last American Leather Chemists Association committee confirmed. These shortcomings of chloroform do not, however, make the results with petroleum ether any more accurate. Results with chloroform may be high; results with petroleum ether may be low.

Considerable interest has been shown lately in the hide powder method of tannin analysis which it is hoped will result in changes making for greater accuracy. Wilson and Kern[1] have proposed quite a departure from the present procedure and have offered data to indicate that the latter may at times be in error to the extent of 200 per cent with some extracts. This and other work has given issue to quite a controversy, the sum and substance of which emphasizes the dire need of an accurate, direct method for determining tannin.

In passing, it is desired to present to you briefly some recent findings which, while not of a chemical nature, are of importance in connection with the physical testing of leather. The influence of relative humidity on the physical properties of paper has been recognized for some time, and testing of paper has therefore been done under controlled conditions of relative humidity and temperature. Of late interest has also been shown in the possible influence of relative humidity in testing other materials. In a recent publication[2] the Bureau of Chemistry has shown

---

[1] *J. Ind. Eng. Chem.*, 1920, 12: 465; *J. Am. Leather Chem. Assoc.*, 1920, 15: 295.
[2] *J. Am. Leather Chem. Assoc.*, 1922, 17: 492.

that, for at least an unfilled, unoiled vegetable tanned leather, the relative humidity exerts an influence surprisingly great. Working at a constant temperature of 70° F. but different relative humidities, extensive data were obtained to show that for an increase of 20 per cent relative humidity, from 35 per cent to 55 per cent, the average increase was 12.9 per cent in tensile strength and 15.7 per cent in elongation; and for an increase of 40 per cent relative humidity, from 35 per cent to 75 per cent, the average increase in tensile strength was 42.3 per cent and in elongation it was 53.1 per cent. You will thus see that humidity exerts a very material influence which can not be safely ignored. While this work was done with only one tannage, there can be little doubt that humidity has a significant effect upon all leathers. It will also be noted from the above figures that the influence of relative humidity was not directly proportional to the increase of the same. That is, for 20 per cent relative humidity the strength gain was 12.9 per cent, while for 40 per cent relative humidity the strength gain was not practically double 12.9, but more nearly three and one-half times as much. The same applies to the elongation figures. In this connection it is interesting to note that the moisture content of the leather pieces, as shown by change in weight at the different relative humidities, was in practically the same relationship. When conditioned at 55 per cent relative humidity the leather showed a gain in weight or moisture of 1.92 per cent, based on the weight at 35 per cent relative humidity, but when conditioned at 75 per cent relative humidity the gain in weight, upon the same basis, was 8.2 per cent, instead of roughly twice 1.92. The importance of this influence of humidity or moisture content of the test samples needs emphasis and more general appreciation; for this reason your referee feels justified in bringing it to your attention.

In conclusion, your referee desires, in order to be absolved of any taint of plagiarism, to emphasize that while the work described has been carried on principally within the American Leather Chemists Association, it is, nevertheless, work in which the scientists of the Bureau of Chemistry, who are members of both the Association of Official Agricultural Chemists and the American Leather Chemists Association have taken and hope to continue to take an active part. As referee, in this association, on a subject in which the other members, while having an inherent interest, have had little opportunity to participate, the writer hopes to be pardoned for this possible digression in presenting a brief review of work largely for another organization and he would like to feel that it has been of more interest than the stereotyped statement, "No report to make".

REPORT ON INSECTICIDES AND FUNGICIDES.

By J. J. T. GRAHAM (Bureau of Chemistry, Washington, D. C.), *Referee*.

The work on insecticides and fungicides for 1922 consisted of a cooperative study of the official distillation method for total arsenic[1] and the hydrazine distillation method[2] on samples of lead and calcium arsenates containing nitrates. Previous work had shown that the official distillation method was not accurate in the presence of nitrates[3], and the hydrazine distillation method, which is unaffected by nitrates, was recommended to take its place. The association, at the 1921 meeting, upon recommendation of the referee, adopted this as a tentative method, but before final action it was necessary that it be submitted to the members for cooperative study.

PREPARATION OF SAMPLES.

Lead arsenate.—Commercial lead arsenate was mixed with a solution of lead nitrate, and the resulting paste evaporated on the steam bath until most of the moisture was expelled. The drying was completed in an electric oven at 105°C. and the sample then ground to pass a No. 40 sieve and thoroughly mixed. The nitrogen content of this sample was shown by analysis to be equivalent to 3.49 per cent of nitrogen pentoxide. The arsenic oxide, determined after heating to fuming with sulfuric acid to destroy the nitrates, was 27.30 per cent.

Calcium arsenate.—Two samples of calcium arsenate were prepared by adding a mixture of arsenic and nitric acids to milk of lime and drying the resulting paste as in the case of lead arsenate. These were ground to pass a No. 40 sieve and were analyzed for nitrogen and arsenic oxide in the same way as the lead arsenate. Sample 1 of calcium arsenate contained 4.74 per cent of nitrogen pentoxide and 40.82 per cent of arsenic oxide, and Sample 2 contained 1.00 per cent of nitrogen pentoxide and 38.75 per cent of arsenic oxide.

Portions of these samples, with the following directions, were sent to 17 laboratories for cooperative work.

DIRECTIONS FOR ANALYSIS.

TOTAL ARSENIC.

REAGENTS.

(a) *Starch indicator.*—Prepare as directed under Paris green[4].

(b) *Standard arsenious oxide solution.*—Prepare as directed under Paris green[4].

(c) *Standard iodine solution.*—Prepare as directed under Paris green[4].

(d) *Hydrazine sulfate and sodium bromide solution.*—Dissolve 20.0 grams of hydrazine sulfate and 20.0 grams of sodium bromide in 1 liter of dilute (1 to 4) hydrochloric acid.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 54.
[2] *J. Assoc. Official Agr. Chemists*, 1922, 5: 402.
[3] *J. Ind. Eng. Chem.*, 1922, 14: 207.
[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 53.

TABLE

Cooperative results on total

ANALYST	CALCIUM ARSENATE, SAMPLE 1			
	Official Distillation Method		Hydrazine Distillation Method	
	Titrated Immediately	Titrated after 24 hours	Titrated Immediately	Titrated after 24 hours
	per cent	*per cent*	*per cent*	*per cent*
J. C. Bubb, Bureau of Chemistry, Washington, D. C.	40.71 40.71	39.94 40.30	41.02 40.91	41.07 40.91
Average	40.71	40.12	40.97	40.99
G. E. Colby, Department of Agriculture, Sacramento, Calif.	34.37	20.17	40.50	40.89
R. P. Cope, Agricultural Experiment Station, Pullman, Wash.	40.58	40.11	40.90	40.93
J. J. T. Graham.	40.82 40.82	40.26 40.21	41.08 41.13	41.08 41.13
Average	40.82	40.24	41.11	41.11
Rosewell Jinkins, Bureau of Chemistry, Washington, D. C.	40.60 40.22	38.48 36.94	40.70 40.60	40.70 40.60
Average	40.41	37.71	40.65	40.65
A. P. Kerr, Agricultural Experiment Station, Baton Rouge, La.	41.55 41.30	32.55 35.02	41.37 41.50 41.55	41.28 41.50 41.61
Average	41.43	33.79	41.47	41.46
W. G. Marshall, Department of Agriculture, Sacramento, Calif.	34.57	20.05	40.33	41.11
A. C. Nothstine, Bureau of Chemistry, Washington, D. C.	39.70 40.78 39.24	37.85 40.01 38.72	40.78 40.88	40.83 40.88 .....
Average	39.91	38.86	40.83	40.86
R. H. Robinson, Agricultural Experiment Station, Corvallis, Ore.	40.77 40.79	40.77 40.80	40.97 41.07 41.10	40.97 41.10 40.96
Average	40.78	40.79	41.05	41.01
R. D. Scott, Department of Health, Columbus, Ohio.	40.43 40.37	37.27 37.88	40.91 40.81	40.85 40.81
Average	40.40	37.58	40.86	40.83
Arthur Shaver, Bureau of Chemistry, Washington, D. C.	39.08 40.23	39.08 40.03	40.99 40.99	40.99 40.99
Average	39.66	39.56	40.99	40.99

*Titrated after 48 hours.
†Titrated after 72 hours.

1.

arsenic, calculated as arsenic oxide.

Calcium arsenate, sample 2				Lead arsenate			
Official Distillation Method		Hydrazine Distillation Method		Official Distillation Method		Hydrazine Distillation Method	
Titrated Immediately	Titrated after 24 hours	Titrated Immediately	Titrated after 24 hours	Titrated Immediately	Titrated after 24 hours	Titrated Immediately	Titrated after 24 hours
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
38.60	38.70	38.81	38.96	27.09	27.02	27.25	27.17
38.70	38.50	38.81	38.86	27.21	26.98	27.21	27.25
38.65	38.60	38.81	38.91	27.15	27.00	27.23	27.21
36.87	27.59	38.40	38.40	23.89	11.66	26.88	27.15
38.66	38.53	38.75	38.75	27.10	26.81	27.18	27.18
38.56	38.61	39.02	39.02	26.92	26.49	27.30	27.30
38.61	38.66	39.02	39.02	26.92	26.03	27.38	27.34
38.59	38.64	39.02	39.02	26.92	26.26	27.34	27.32
39.06	38.58	38.77	38.77	27.20	25.75	27.34	27.41
38.87	37.90	38.77	38.77	26.83	25.03	27.41	27.56
38.97	38.24	38.77	38.77	27.02	25.39	27.38	27.49
38.47	35.75	39.10	39.12	24.74	19.09	27.38	27.40
.....	.....	39.16	39.22	24.81	19.50	27.45	27.50
.....	.....	.....	.....	.....	.....	27.38	27.35
38.47	35.75	39.13	39.17	24.78	19.30	27.40	27.41
37.00	25.10	38.60	38.70	34.18	12.00	26.88	27.15
38.11	37.54	38.72	38.72	26.62	25.77	27.00	27.04
38.31	36.46	38.72	38.72	26.96	26.11	27.08	27.04
37.90	37.54	38.62	38.62	26.04	19.33	.....	.....
38.11	37.18	38.69	38.69	26.54	23.74	27.04	27.04
38.52	38.50	38.85	38.88	27.02	27.02	27.18	27.18
38.54	38.51	38.83	38.83	26.91	26.95	27.18	27.21
.....	.....	.....	.....	.....	.....	.....	.....
38.53	38.51	38.84	38.86	26.97	26.99	27.18	27.20
38.49	38.19	38.51	38.45	26.66	26.08	26.94*	26.94*
38.42	37.94	38.55	38.55	26.69	24.47	26.94†	26.94†
38.46	38.07	38.53	38.50	26.68	25.28	26.94	26.94
36.89	36.79	38.79	38.79	26.69	26.69	27.26	27.26
38.70	38.70	38.79	38.79	26.12	26.12	27.26	27.26
37.80	37.75	38.79	38.79	26.41	26.41	27.26	27.26

TABLE

Cooperative results on total

ANALYST	CALCIUM ARSENATE, SAMPLE 1			
	Official Distillation Method		Hydrazine Distillation Method	
	Titrated Imme-diately	Titrated after 24 hours	Titrated Imme-diately	Titrated after 24 hours
	per cent	*per cent*	*per cent*	*per cent*
W. A. Stone, Agricultural & Mechanical College, College Station, Tex.	40.12	24.36	40.72	40.72
	40.13	26.08	40.72	40.72
	39.21	.....	40.72	.....
	38.45	.....	40.73	.....
Average	39.48	25.22	40.72	40.72
L. R. Streeter, Agricultural Experiment Station, Geneva, N. Y.	41.85	40.70	42.35	42.35
	41.80	39.06	42.40	42.40
	.....	.....	42.40	.....
	.....	.....	.....	.....
Average	41.83	39.88	42.38	42.38
E. R. Tobey, Agricultural Experiment Station, Orono, Maine.	40.44	38.77	40.39	40.35
O. B. Winter, Agricultural Experiment Station, E. Lansing, Mich.	41.08	40.27	41.09	40.89
	40.90	.....	40.90	41.28
	40.90	.....	40.90	.....
Average	40.96	40.27	40.96	41.09
General averages	39.76	35.54	40.94	41.02
Referee's analysis after destroying nitrates	40.82	.....	.....	.....
‡J. J. Taylor, Department of Agriculture, Atlanta, Ga.	41.02	40.23	40.99	41.09
	40.90	40.19	41.09	41.09
Average	40.96	40.21	41.04	41.09

‡Received after report was completed.

DETERMINATIONS.

Hydrazine distillation method.

Weigh 1.5 grams of calcium arsenate (or 2.0 grams of lead arsenate) and transfer to a distilling flask. Add 50 cc. of the hydrazine sulfate and sodium bromide solution and close the flask with a stopper through which passes the stem of a dropping funnel. Connect to a well-cooled condenser, the delivery end of which is attached to the system of flasks used in the official distillation method[1], omitting the third flask. Boil for 2 or 3 minutes and then add 100 cc. of concentrated hydrochloric acid by means of the dropping funnel and distil until the volume in the distilling flask is reduced to about 40 cc; add an additional 50 cc. of concentrated hydrochloric acid and continue the distillation until the contents of the flask are again reduced to about 40 cc. Wash down the con-

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 54.

1—*Continued.*

arsenic, calculated as arsenic oxide.

CALCIUM ARSENATE, SAMPLE 2				LEAD ARSENATE			
Official Distillation Method		Hydrazine Distillation Method		Official Distillation Method		Hydrazine Distillation Method	
Titrated Immediately	Titrated after 24 hours	Titrated Immediately	Titrated after 24 hours	Titrated Immediately	Titrated after 24 hours	Titrated Immediately	Titrated after 24 hours
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
38.23	33.07	38.68	38.67	26.52	15.24	27.03	27.03
37.94	34.75	38.67	38.67	26.48	14.32	27.03	27.03
37.95	.....	38.68	.....	25.77	.....	27.04	.....
37.70	.....	38.67	.....	25.59	.....	27.03	.....
37.96	33.91	38.68	38.67	26.09	14.78	27.03	27.03
39.34	39.20	39.45	39.50	27.60	27.25	27.80	27.80
39.35	38.90	39.45	39.44	27.45	27.15	27.80	27.75
39.40	39.30	.....	.....	27.40	27.10	27.75	.....
39.65	39.40	.....	.....	27.30	.....	.....	.....
39.44	39.20	39.45	39.47	27.44	27.17	27.78	27.78
38.72	36.69	38.63	38.55	26.85	25.25	26.92	26.75
38.98	34.94	38.78	38.78	26.93	26.35	27.07	27.07
38.88	38.40	38.78	38.98	27.07	26.35	27.07	27.21
.....	.....	.....	.....	27.07	.....	.....	.....
38.93	36.67	38.78	38.88	27.02	26.35	27.07	27.14
38.34	36.03	38.79	38.81	26.34	22.96	27.17	27.20
38.75	.....	.....	.....	27.30	.....	.....	.....
39.03	38.65	39.01	39.01	27.36	27.07	27.59	27.78
39.08	38.69	38.91	38.91	27.27	27.12	27.59	27.70
39.06	38.67	38.96	38.96	27.32	27.10	27.59	27.74

denser, transfer the contents of the receiving flasks to a 1-liter graduated flask, make to volume and mix thoroughly. Pipet a 200 cc. aliquot into a 500 cc. Erlenmeyer flask and nearly neutralize with a 40% solution of sodium hydroxide, using phenolphthalein as indicator and keeping the flask well cooled. If the neutral point is passed, add hydrochloric acid until again slightly acid. Finish the neutralization with sodium bicarbonate, add 4–5 grams in excess, and titrate with standard iodine solution using starch solution as indicator. Calculate the results in terms of arsenic oxide.

NOTE.—If more convenient, the receiving flasks may be cooled by running water during the distillation instead of the cracked ice as shown in the illustration[1].

Make determinations by both methods on each of the three samples, titrating as soon as possible after the distillation. Report the time elapsed between the end of the distillation and the titration of the distillates. Allow all the distillates to stand for 24 hours and again titrate aliquots of each.

Reports from ten laboratories are shown in Table 1.

[1] *Assoc. Official Agr. Chemists, Methods,* 1920, 54.

COMMENTS BY ANALYSTS.

George E. Colby and W. G. Marshall.—On the lead arsenate the nitrates appear to throw the official method out somewhat in direct proportion to their content.

On Sample 1 of calcium arsenate, with the highest nitrates of the series, the official method appears to yield only about 80% of the arsenic oxide present, as set by the hydrazine test.

On Sample 2 of calcium arsenate, containing the least quantity of nitrate, the result by the official test is out only about 5%.

It is obvious that the official method of distillation for total arsenic oxide is not generally applicable in the presence of nitrates, but it is unlikely that commercial samples of arsenate of lead or calcium will often be found in the market with such quantities of nitrates as this series of arsenates.

R. P. Cope.—Heat is produced in the neutralization of the hydrochloric acid, and the time necessary for cooling may give opportunity in the official method for additional oxidation by any nitrates present. The hydrazine method is more pleasant to run.

R. H. Robinson.—Titrations on all determinations were made as soon as possible after the distillation, which was about 15 minutes. After allowing to stand 24 hours, titrations were again made. No differences were observed after standing 24 hours at about 20°C. No trouble was experienced with the hydrazine distillation method, and excellent checks were obtained in the duplicate determinations. Since the receiving flasks were cooled by running water at 10°C. instead of with packed ice, it was necessary to exercise care in watching that there was no loss of the copious fumes that came over in the official distillation method. This precaution was not necessary in the hydrazine distillation method.

R. D. Scott.—The hydrazine method is evidently more satisfactory than the official method in the presence of nitrates. A slightly higher blank was noted with the hydrazine method than with the official method.

E. R. Tobey.—The reagents submitted by the referee were used. The arsenious oxide was heated 5 hours at 105°C. before the portion used in standardization was weighed out. From the standpoint of manipulation the hydrazine sulfate method is preferable.

O. B. Winter.—The two methods check very closely. The time which elapses between the distillation and the titration causes no change in the results by the hydrazine method but gives rise to a slight loss by the official method. The hydrazine method requires somewhat less time for the distillation.

DISCUSSION.

The most striking fact shown by the results in the table is the unreliability of the official distillation method in the presence of nitrates. Of 15 analysts participating in this work, only two obtained as high results by the official method as they obtained by the hydrazine method. Two analysts obtained distillates which gave good checks when titrated immediately, and after a period of 24 hours; but the distillates obtained by all other analysts gave lower results after standing for that period. No uniformity, however, is shown in the rate of change in the results on standing. The loss of arsenic in the distillates varied among the different analysts from a few tenths of a per cent to 50 per cent of the arsenic present. In contrast to this, is the uniform behavior of the distillates from the hydrazine method. With two exceptions, the

titrations at the end of 24 hours checked those obtained immediately after distillation, and the results not only agreed well among themselves, but they checked the results obtained by the referee using the official distillation method on charges in which the nitrates were destroyed before the analysis was made.

The only objection to the use of the hydrazine method is the increased cost of hydrazine sulfate over cuprous chloride, and this is somewhat offset by the saving in the quantity of hydrochloric acid used. Hydrazine sulfate can be made in the laboratory with very little trouble and expense by the action of sodium hypochlorite on ammonia water[1].

SUGGESTIONS FOR FUTURE WORK.

A number of insecticides and fungicides known by the general term of dusting mixtures are now on the market. These preparations vary considerably in their formulae, but usually consist of two or more of the following substances: lead arsenate, calcium arsenate, Paris green, Bordeaux mixture, sulfur, lime, calcium sulfate, kaolin, tobacco powder and nicotine. The association has adopted no methods for the analysis of these mixtures, and the referee suggests that a study be made of methods for this class of compounds.

RECOMMENDATIONS.

It is recommended—

(1) That the mercury-thiocyanate method for zinc oxide in zinc arsenite as given in the referee's report for 1921[2] be adopted as an official method.

(2) That the method (1) for the determination of calcium oxide in calcium arsenate as given in the referee's report for 1921[3] be adopted as an official method.

(3) That the method (2) for the determination of calcium oxide in calcium arsenate as given in the referee's report for 1921[4] be adopted as an official method.

(4) That in the "General procedure for the analysis of a product containing arsenic, antimony, lead, copper, zinc, iron, calcium, magnesium, etc.", the method for zinc oxide as given in the referee's report for 1921[5] be adopted as an official method.

(5) That the hydrazine distillation method for the determination of total arsenic[6] be adopted as an official method.

[1] University of Illinois Bull., 1920, 18: 6.
[2] *J. Assoc. Official Agr. Chemists*, 1922, 5: 392.
[3] *Ibid.*, 395.
[4] *Ibid.*, 396.
[5] *Ibid.*, 398.
[6] *Ibid.*, 403.

REPORT ON SOILS.

By W. H. MacIntire (Agricultural Experiment Station, Knoxville, Tenn.), *Referee.*

No particular problem has been under investigation during the past year. The Committee on Revision of Methods for Soil Analysis expects to make further report and recommendations at the next meeting of the association. It was, therefore, thought advisable to await such action before undertaking additional work under the general heading of "Soils".

REPORT ON SULFUR IN SOILS.

By W. H. MacIntire, *Associate Referee* and W. M. Shaw (Agricultural Experiment Station, Knoxville, Tenn.).

The work upon sulfur in soils during the past year has been directed toward the study and perfection of technique which will afford complete oxidation of all forms of sulfur in soils and insure complete removal of the oxidation products from the soil mass. Pursuing further the study of the digestion of soils in nitric acid, the plan has been to adapt the procedure to charges of sufficient bulk to insure workable quantities of the sulfate precipitate, even from soils of very low total sulfur content. With this basic thought, the collaborative work was planned to determine (1) the length of time required for the digestion of soil with concentrated nitric acid; (2) the probability of occlusion of sulfates in the ammoniacal precipitation and reprecipitation of iron; and (3) the possible interference of native soil barium which may be dissolved from some soils by the process of acid digestion.

The following outline of procedure was sent out to those who expressed willingness to collaborate:

Concentrated Nitric Acid Method of Procedure for the Determination of Total Sulfur in Soils.

Introduce 50 grams of soil low in organic matter, or 25 grams of soil high in organic matter, into a 500 cc. Kjeldahl flask. Insert a small funnel in the neck of the flask. Add about 125 cc. of concentrated nitric acid; heat slowly and boil for 1 hour. Follow the same procedure in parallel, by boiling for a 2-hour period and also for 3 hours. Cool, dilute to 400 cc. and pour off the clear liquid through a Büchner funnel. Add 250–300 cc. of hot water; agitate; throw upon Büchner and wash with hot water to a combined volume of 1 liter. Evaporate filtrate to dryness at a low temperature. Add 10 cc. of concentrated hydrochloric acid and again evaporate. Repeat the addition of, and evaporation with, hydrochloric acid. Take up with a few drops of hydrochloric acid; bring into solution and precipitate iron, by addition of 1 to 1 ammonium hydroxide, from a volume of 400 cc. Pour onto a Büchner and wash twice. Transfer the filter to original beaker; dissolve; macerate the filter and again precipitate from a volume of

about 300 cc. and filter into original filtrate, washing to a volume of 1 liter. Acidify filtrate with a slight excess of hydrochloric acid; concentrate to a volume of 400 cc; add hot barium chloride (1+9) and agitate vigorously. Permit barium sulfate to stand 18 hours and filter through an acid-washed asbestos Gooch filter. Report as grams of barium sulfate.

NOTE.—In studying this method it would be well to add a *small amount of freshly precipitated barium sulfate* to the soil prior to the digestion and determine the point at which it may be lost to the procedure, in order to ascertain what may be expected from any barium sulfate formed during the digestion because of the occurrence of barium compounds native to the soil. The method should also be tested by the addition of known amounts of sodium, potassium, calcium and magnesium sulfates.

COLLABORATIVE RESULTS.

A. L. Prince, New Jersey Agricultural Experiment Station.—The influence of length of the period of nitric acid digestion was tried out at this station, using a 50-gram charge of acid silt loam. The results are given in Table 1.

TABLE 1.

Barium sulfate determined from nitric acid soil extract.

	1-hour digestion	2-hour digestion	3-hour digestion
	gram	*gram*	*gram*
A	0.0802	0.0665	0.0750
B	0.0816	0.0762	0.0778
Average....	0.0809	0.0714	0.0764

Assuming all other conditions constant, it is evident that boiling with nitric acid for one hour will produce a sulfate yield as great as that brought about by boiling for a period of 3 hours. No results were reported on a fortified soil.

D. E. Bullis, Oregon Agricultural Experiment Station.—The results from the Oregon station as to the influence of time upon the completeness of oxidation of the soil sulfur, from a Williamette loam are given in Table 2.

TABLE 2.

Barium sulfate determined from nitric acid soil extract.

	1-hour digestion	2-hour digestion	3-hour digestion
	gram	*gram*	*gram*
A	0.0406	0.0338	0.0344
B	0.0397	0.0355	0.0389
Average....	0.0402	0.0347	0.0367

Again, as in the case of the New Jersey results, the highest sulfate determinations were secured from the solution derived from a 1-hour

digestion. These analyses were carried out by the elimination of iron through ammoniacal precipitation. It is quite probable that less iron was dissolved during the 1-hour digestion than during the digestion for the longer periods; and since, as will be shown by results from the referee's laboratory, the amount of iron influences the extent of occlusion, a smaller iron occurrence in the 1-hour digestion may be responsible for the larger sulfate yield obtained from the solution digested for that period of time.

TABLE 3.

Barium sulfate fraction received from that added to a 25-gram charge of soil.

	1-hour digestion		2-hour digestion		3-hour digestion	
	A	B	A	B	A	B
	gram	*gram*	*gram*	*gram*	*gram*	*gram*
Soil +.0963 gm. $BaSO_4$	0.0735	0.0681	0.0761	0.0743	0.0713	0.0747
Soil alone (average).	0.0401	0.0401	0.0346	0.0346	0.0366	0.0366
$BaSO_4$ recovered....	0.0334	0.0280	0.0415	0.0397	0.0347	0.0381
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Recovery..........	34.7	29.1	43.1	41.2	36.0	39.7
Recovery calculated to barium in soil..	0.0816	0.0684	0.1013	0.0969	0.0846	0.0934

In Table 3 are given the results reported from the Oregon station relative to the carry-through of barium sulfate which may be formed during the acid digestion as a result of occurrences of native barium in soil. From additions of 0.0963 gram of freshly precipitated barium sulfate respective recoveries of 31.9 per cent, 42.2 per cent and 37.9 per cent were secured after 1-, 2-, and 3-hour digestions of soil and additions. These respective recoveries calculate to native barium occurrences of 0.0750 per cent, 0.0991 per cent and 0.0890 per cent. No data showing such extensive amounts of barium present in soils were found. The foregoing results are in harmony with those secured by the referee and associates and indicate that the amounts of barium occasionally to be found in soils would not interfere with the accuracy of the method, if it should prove otherwise adaptable.

W. M. Shaw, University of Tennessee Agricultural Experiment Station.—Duplicate digestions were made of fairly fertile loam soil for periods of 1 hour, 2 hours and 3 hours, according to the outline previously given. Fifty-gram charges of soil alone and soil fortified with calcium sulfate equivalent to 0.0845 gram of barium sulfate were used in the digestions. Iron was eliminated through double precipitation. Ammoniacal salts were removed by evaporation with nitric acid and two evaporations with hydrochloric acid, prior to the barium sulfate precipitation from a nitrate-free solution. The following results were obtained:

TABLE 4.

Barium sulfate determined—gram per 50 grams of soil.

	1-hour digestion	2-hour digestion	3-hour digestion
	gram	*gram*	*gram*
Soil only....................	0.0454	0.0483	0.0444
Soil plus calcium sulfate equivalent to 0.0845 gram of barium sulfate....................	......	......	0.1079

From these results it would appear that a 1-hour digestion period is as effective as one continued for two additional hours. It is also apparent that but 0.0625 gram of barium sulfate equivalent of the 0.0845-gram addition was recovered. This represents a recovery of approximately 74 per cent of the addition. The data do not demonstrate, however, whether the partial recovery was due to incomplete washing out of sulfates from the acid insoluble residue, or to their occlusion in the ammoniacal precipitate of hydrated iron oxide. The results of experiences with the thorough washing with acid and hot water through the thin soil layer upon the Büchner indicated that the first assumption is hardly tenable. The probability of occlusion of sulfates in the hydrated iron precipitate was therefore studied. Sulfates were determined separately in the filtrate from the first ammoniacal precipitation and also in the filtrates from the second and third re-precipitations.

No variable was introduced during precipitation of barium sulfate because of the presence of different amounts of ammoniacal salts; each filtrate was freed of ammonium chloride by evaporation with nitric acid, nitrates being then eliminated by two evaporations with concentrated hydrochloric acid, prior to the taking up with dilute hydrochloric acid, from which solution the sulfates were precipitated. The results obtained are given in Table 5.

TABLE 5.

Barium sulfate determinations upon separate filtrates from three hydrated iron precipitates.

Soil only—50-gram charge	Analysis A	Analysis B	Average
	gram	*gram*	*gram*
In first filtrate..........................	0.0345	0.0325	0.0335
In second filtrate..........................	0.0106	0.0158	0.0132
In third filtrate..........................	0.0110	0.0065	0.0088
Total..........................	0.0561	0.0548	0.0555
Soil—50 grams plus magnesium sulfate equivalent to 0.1300 gram of barium sulfate			
In first filtrate..........................	0.1057	0.0914	0.0986
In second filtrate..........................	0.0449	0.0565	0.0507
In third filtrate..........................	0.0248	0.0251	0.0250
Total..........................	0.1754	0.1730	0.1742

When from the average total of 0.1742 gram of barium sulfate obtained from the fortified soil, is subtracted the barium sulfate average of 0.0555 gram recovery—inclusive of the blank from the unfortified soil—0.1187 gram of barium sulfate is found, or a recovery of 91.3 per cent of the sulfate addition. Since the barium sulfate yield from the filtrate from the third ammoniacal precipitation is about three times that from the third and corresponding filtrate from the unfortified soil it would appear that this discrepancy is accounted for by occlusion of the sulfate in the mass of hydrated iron oxide thrown down the third time. In round numbers, the recovery from each successive filtration is about one-half that secured in the respective preceding filtrate, for both soil and fortified soil. The occlusion was further studied by means of a synthetic soil solution of the following composition per 100 cc.

	gram
Iron and aluminium oxides	6.063
Calcium oxide	1.250
Magnesium oxide	1.250
Potassium oxide	0.500
Sodium oxide	0.500

In using 100 cc. aliquots of this synthetic solution, to which magnesium sulfate was added, in equivalence to 0.1300 gram of barium sulfate, iron and aluminium were removed by three ammoniacal precipitations from the larger volume of 400 cc., rather than a volume of 200 cc., which was used in the previous work with the soil extractions. The sulfate determinations were made upon the combined filtrates, ammoniacal salts having been first eliminated. It was thought possible to decrease the occlusion to a minimum through the greater dilution. The results are given in Table 6.

TABLE 6.

Barium sulfate recovered from 0.1300 gram of barium sulfate equivalent of magnesium sulfate.

	Analysis A	Analysis B	Average
	gram	*gram*	*gram*
Barium sulfate in aggregate of three filtrations	0.1088	0.1083	0.1085
Barium sulfate in aggregate blank	......	......	0.0268
Corrected barium sulfate recovery			0.0817
Amount unrecovered			0.0483

It is evident from these results that the increase in volume was not sufficient to eliminate extensive occlusion of sulfates by the hydrated oxides, even with three ammoniacal precipitations. The same number of ammoniacal precipitations were carried out upon another set of synthetic aliquots, the 100 cc. aliquot first having been made to a volume

of 800 cc. In this instance, the three filtrates were analyzed separately in duplicate. The separate sulfate determinations and totals are given in Table 7.

TABLE 7.

Barium sulfate recovered in each filtrate from three ammoniacal precipitations.

	Analysis A	Analysis B	Average
	gram	*gram*	*gram*
In first filtrate	0.0804	0.0830	0.0817
In second filtrate	0.0502	0.0405	0.0453
In third filtrate	0.0160	0.0208	0.0184
Total	0.1466	0.1443	0.1454
Total reagent blank			0.0268
Total correct recovery of added barium sulfate equivalent			0.1186
Barium sulfate equivalent of sulfates, unrecovered from three filtrates			0.0114

From these results it is apparent that three precipitations of iron and aluminium will not afford a complete yield of the added sulfates to the several filtrates from the masses of the hydrated oxides of the two elements, in the diminished concentration effected by increasing the volume of aliquots from 100 cc. to 800 cc. It is apparent, however, that the greater dilution has been effective in causing a distinct diminution in the amounts of sulfates occluded.

Influence of amount of iron and aluminium upon sulfate occlusion.

The influence of the bulk of the hydrated iron and aluminium upon the amounts of sulfate occluded was studied by the use of different aliquots of the synthetic soil solution, each made to a volume of 400 cc. before removal of iron and aluminium, through two precipitations by additions of ammonium hydroxide, with a constant addition of magnesium sulfate, equivalent to 0.1300 gram of barium sulfate, but with a necessarily varying reagent blank.

TABLE 8.

Barium sulfate recoveries from iron and aluminium variables and barium sulfate constant.

Synthetic solution		Analysis A	Analysis B	Average
cc.	*grams*	*gram*	*gram*	*gram*
100	6.063 ferric and aluminic oxide	0.0972	0.0910	0.0941
50	3.032 ferric and aluminic oxide	0.1173	0.1173	0.1173
25	1.516 ferric and aluminic oxide	0.1260	0.1248	0.1254

From these data it will be seen that the 100 cc. aliquot, carrying 6.063 grams of ferric-aluminic oxides was responsible for an occlusion of

0.0359 gram of barium sulfate equivalent; the 50 cc. aliquot, containing 3.032 grams of the oxides of the two elements caused an occlusion of 0.0127 gram of barium sulfate equivalent, while the 25 cc. aliquot, carrying but 1.516 grams of the two oxides, induced an occlusion of only 0.0046 gram barium sulfate equivalent. Each gram of the two oxides would appear to have effected occlusion of 0.0059 gram, 0.0042 gram and 0.0030 gram, respectively, in each of the three diminishing aliquots. It is evident from these results that the amount of iron and aluminium present in a soil would have a very important bearing upon the recovery of sulfates from its nitric acid digestion. It is quite possible that the hydrated oxides of iron and aluminium may vary decidedly in their ability to occlude. However, the two elements occur in parallel, if in varying proportions, in all soils, and their properties need not be considered separately for the purpose at hand.

Precipitation of barium sulfate without elimination of iron and aluminium.

It is generally recognized that the presence of ferric chloride is detrimental to the determination of barium sulfate, more especially when the precipitate is filtered by gravity through paper. C. B. Williams[1] has shown that sulfate results are much higher when iron is eliminated by ammoniacal precipitation than when the precipitations are made without such elimination. It has not been made altogether clear whether the cause may be assigned to the minus error introduced by the presence of a double sulfate, as maintained by Talbot[2], or to the solvent action of ferric chloride upon the barium sulfate precipitate. The difficulty of removing all iron from the filter was not encountered in these studies, since an asbestos Gooch was used for all the barium sulfate determinations, except those from the 1 liter volume. It was thought possible to vary the volume and temperature of the barium sulfate precipitation, in the presence of a constant amount of iron, so as to effect conditions which would permit of complete sulfate recovery without the interference of the ferric salts. Aliquots of 100 cc. of the synthetic solution carrying a barium sulfate equivalence of 0.1300 gram were used. The several duplicates were diluted to 250 cc. and 1000 cc. in the cold and barium sulfate precipitations made and permitted to stand for 18 hours.

TABLE 9.

Barium sulfate recovered by precipitation in the cold from dilutions of 100 cc. aliquot of synthetic solution.

Aliquot	Analysis A	Analysis B	Average
	gram	*gram*	*gram*
100 cc. diluted to 250 cc.	0.1532	0.1490	0.1511
100 cc. diluted to 1000 cc.	0.1241	0.1204	0.1223

[1] *J. Am. Chem. Soc.*, 1902, 24: 658.
[2] Talbot, H. P., Quantitative Chemical Analysis, 1908.

These analyses might be taken to indicate either an incomplete precipitation from the larger volume at room temperature, or else a greater solvent action of the ferric and aluminic chloride in the more dilute solution. However, after ignition, the barium sulfate precipitate from the smaller volume carried much more iron than that from the larger volume. Again, it is quite probable that the occlusion of salts of calcium, magnesium, sodium and potassium in the barium sulfate precipitate was much greater in the case of the precipitation from the more concentrated solution.

The effect of temperature upon the precipitation was observed by making precipitations at room temperature and at boiling, using a 100 cc. aliquot of the synthetic soil solution and making to a volume of 250 cc. in each case. The results so obtained are given in Table 10.

TABLE 10.

Precipitation of barium sulfate from constant volume of synthetic solution at room temperature and at boiling, without removal of iron and aluminium.

Aliquot	Analysis A	Analysis B	Average
	gram	*gram*	*gram*
100 cc. diluted to 250 cc. cold	0.1532	0.1490	0.1511
100 cc. diluted to 250 cc. hot	0.1468	0.1401	0.1434

The barium sulfate recoveries from the cold solution containing ferric and aluminic chlorides are appreciably heavier than those made by precipitation at boiling temperature. The precipitates from the cold solution being finer than the more granular ones from the hot solution, it would be expected that they would occlude larger amounts of the alkali and alkali-earth bases. However, it was not possible to repeat and amplify this phase of the work.

Repetition of nitric acid digestion of soil residues.

After the compilation of the data obtained by collaboration, additional work was done relative to the influence of the period of digesting soil with concentrated nitric acid. In the later work the effect of repetition of boiling after removal of the digestant by filtration was tried instead of continued boiling for a longer period, as was done in the earlier work. After boiling for one hour the insoluble residue was thrown upon a Büchner and the thin layer of soil thoroughly washed with hot water. The residue was then returned to the Kjeldahl and the digestion, filtration and washing repeated. Iron and aluminium were removed by four precipitations. The first three ammoniacal filtrates were combined and analyzed for sulfates. The sulfate content of the fourth filtration from the iron and aluminium precipitation was also determined. The data of Table 11 represent the determinations after application of the several blanks for reagent.

TABLE 11.

Barium sulfate determination upon nitric acid digestion for one hour and upon repetition of the digestion of insoluble residues.

	Loam soil		Clay subsoil	
	A	B	A	B
	gram	gram	gram	gram
First extraction, 3 filtrates	0.0577	0.0655	0.0454	0.0383
First extraction, 4th filtrate only	0.0030	lost	0.0032	0.0050
First extraction, 4 ammoniacal filtrates	0.0607	......	0.0486	0.0433
Repetition extraction, 3 filtrates	0.0162	0.0172	0.0079	0.0104
Repetition extraction, 4th filtrate only	0.0003	*0.0002	0.0005	0.0004
Repetition extraction, 4 ammoniacal filtrates	0.0162	0.0172	0.0084	0.0108

*Considered as identical with reagent blank.

The data of Table 11 demonstrate that the amounts of native sulfur recovered by two hours of digestion are greater than those recovered by a digestion of but one hour, when filtration is carried out after the first hour's boiling. The repetition of digestion differs in this respect from the continuous boiling for the longer period. The results obtained are also relatively different, for continued boiling for the 2-hour and 3-hour periods failed to produce any greater yield of sulfates than was obtained in the 1-hour period. It would appear that either the extent of oxidation of sulfureous materials is greater after two hours, or else the variation in the method of extraction is responsible for a greater recovery from equal amounts of end-products.

MISCELLANEOUS.

Additional work was also done in an attempt to remove iron by a feasible procedure, other than precipitation in a gelatinous bulk characteristic of the iron and aluminium precipitation. The following technique was carried out:

The nitric acid extract was evaporated to near dry condition, diluted, neutralized with ammonia and the iron precipitated by hydrogen sulfide. The sulfide was then quickly filtered and the ammoniacal solution containing ammonium sulfide, calcium sulfide, magnesium sulfide, thiosulfates and sulfates was acidified, boiled and filtered. The filtrate was concentrated and excess ammonium salts removed by evaporation with nitric acid. The residue was twice taken up and evaporated with concentrated hydrochloric acid and the sulfates precipitated from a dilute hydrochloric acid take-up.

The results secured were high owing to thiosulfate and some sulfate formations during the procedure. The method appears worthy of some study, however, since it may be that a small correction, secured as a blank, will enable the analyst to obtain results very close to the absolute.

The variation in the iron occurrences does not affect this method, differing therein from the removal of that element by ammoniacal precipitation.

It is apparent from the data submitted that the usual method of precipitation of iron and aluminium prior to the determination of sulfates—ammonium chloride having been eliminated—will not permit of the complete recovery of sulfates present. It is, furthermore, patent that the proportion of iron to sulfate and the volume from which the ammoniacal precipitation is made are factors of moment as vitiating influences. Using the figures obtained relative to the amounts of sulfates precipitated from a volume of 250 cc., as compared with those from a volume of 100 cc., with a constant amount of iron, it is quite possible that a definite concentration may obtain, at which point the absolute amount of barium sulfate recoverable may be precipitated.

RECOMMENDATION.

It is recommended that further study be made in an effort to secure a mode of procedure which may be used in removing all the sulfates which are carried by a nitric acid soil, or synthetic soil, solution.

E. T. Wherry: May I say a word about the hydrogen ion concentration? It is being determined more on soils than on other agricultural chemical products. So many methods are published that it is very difficult in starting out in this work to determine which method to use. It seems to me this association should study the subject and have a referee not only for soil but for all agricultural products in which it is expected to determine active acidity—for instance, in plant juices, extracts of plants and dried plant tissue and nutritive media, etc. So if it is in order, I should like to make a motion that this association appoint such a referee, namely, on the determination of active acidity or hydrogen ion concentration for agricultural chemical products.

The motion was seconded and carried.

EFFECT OF CROPPING UPON THE ACTIVE POTASH OF THE SOIL.

By G. S. Fraps (Agricultural Experiment Station, College Station, Texas).

The active phosphoric acid or active potash of the soil is that soluble in 0.2N nitric acid. A method for this determination was worked out by various referees of this association and incorporated in previous methods, but it was removed by the Committee on Revision of Methods of Soil Analysis.

It has been shown that the potash removed by crops from soils in Texas pot experiments was related to the active potash of the soil[1] and that a similar relation holds for minerals containing potash and the potash taken from them by plants[2].

It has also been shown that the active potash is less after the soil has been cropped than before cropping[1]. Further study of this relation is reported in this paper.

METHOD OF WORK.

The crops were grown in pots containing 5000 grams of soil, to which phosphoric acid and nitrogen were added so that the size of the crop would be limited by potash and not by phosphoric acid or nitrogen. Corn and sorghum were grown, in some cases for only one year, and in other cases for several years in succession. The crops were harvested, weighed, and their potash content estimated. The estimation of the potash in the crops is absolutely necessary, for the reason that wide variations occur in the percentages of potash in plants grown on different soils. Some crops may contain less than one per cent of potash, while others may contain over seven per cent. The active potash of the soil has a great effect upon the percentage of potash present in the crop, as shown in Bulletin 145.

At the end of the experiment the soils in the pots were prepared for analysis, and the active potash was estimated. The decrease in active potash is the difference in the amount present before and after cropping.

The soils were arranged in groups according to the potash removed by the crops, and the decrease of active potash tabulated and averaged. The average results with 409 samples are given in Table 1.

TABLE 1.

Effect of cropping on active potash lost in the soil.

GROUPS—POTASH REMOVED	POTASH IN CROPS	DECREASE IN ACTIVE POTASH	DECREASE IN ACTIVE POTASH DIVIDED BY POTASH IN CROPS	NUMBER OF SOILS AVERAGED
Parts per million	*Parts per million*	*Parts per million*	*per cent*	
0–50	39	17	43.6	19
51–100	78	30	38.4	59
101–200	148	61	41.2	153
201–300	242	100	41.3	77
301–400	348	153	43.7	39
401–500	451	199	44.1	20
501–600	552	212	38.4	18
601–700	641	195	30.4	15
701–800	741	201	27.1	3
801–900	882	577	65.4	3
901–1000	964	338	35.0	3

[1] Texas Agr. Expt. Sta. Bull. 145.
[2] *Ibid.*, 284.

The relation between the potash removed by the crops and the decrease of potash from the soil was also studied by statistical methods. For this purpose a correlation table was prepared, and the factors of correlation were calculated. The correlation factor between potash removed by the crops and the active potash removed from the soil, R, is 0.7219 ± 0.0160. The nearer this factor approaches ± 1, the better is the correlation. These figures show that there is a close relation between the potash removed from the soil and the decrease of active potash in the soil.

The decrease of active soil potash should not equal the potash removed by the crops. If a soil is subjected to several successive treatments with 0.2N acid, the amount of potash removed becomes smaller with each successive extraction, but in no case does it become zero. If a crop removed all the active potash represented by the first extraction, there would still remain the amount of active potash obtainable in a second extraction. For this reason, the decrease of active soil potash could only be a fraction of the amount of potash removed by the plants, and the size of this fraction would vary with different soils.

The fact that the active potash of the soil is reduced by cropping is further evidence of the importance of the determination of the active potash in the soil analysis. It has already been shown that the amount of potash removed by the crops is related to the active potash present in the soil. These two lines of experimental evidence are favorable to the use of the determination of active potash in the soil analysis. The fact that active potash is reduced by cropping should also be of importance in connection with the study of field experiments on potash, but the matter is badly complicated by the difficulty in securing proper samples of the soil cropped. It is an easy matter to secure representative samples of soil used for experiments in pot work, but it is very difficult to sample a field so as to represent accurately the character of the soil. This matter of sampling of land has not received the attention that it deserves. The effect of the subsoil is also difficult to allow for. It is probable that many results of chemical studies of field work are complicated and obscured through the use of samples which did not really represent the situation.

CONCLUSION.

The potash removed by crops, in pot experiments, is related to the active potash of the soil; and the decrease of active soil potash is related to the potash removed by the crops.

REPORT ON FOODS AND FEEDING STUFFS.

By J. B. REED (Bureau of Chemistry, Washington, D. C.), *Referee.*

The committee recommended that the Referee on Foods and Feeding Stuffs study methods for the determination of ether extract in various foods and feeding stuffs this year with the view to ascertaining whether or not the official method for the determination of ether extract[1] is applicable to all the products for which it is now being used.

Ether extract determinations were made by the official method and by the C. R. Smith method[2] on entire wheat and the various products and by-products obtained in the milling of wheat into flour. The average results obtained by the two methods are shown in Table 1.

TABLE 1.
Results of ether extract determinations comparing two methods.

Product	Official method	C. R. Smith method
	per cent	*per cent*
Entire wheat	1.77	2.33
First break stream	0.62	1.09
Second break stream	0.71	1.17
First middlings stream	0.86	1.38
Second middlings stream	0.82	1.37
Middlings (semolina)	1.07	1.65
Bran	2.91	3.01
Shorts (standard middlings)	4.33	4.51

These results indicate that the use of the more complicated and expensive Smith method is not warranted in making ether extract determinations on bran and shorts, since the less complicated official method gives practically the same results.

The collaborative work of this investigation was done by L. E. Bopst, assisted by C. E. Goodrich, both of the Bureau of Chemistry, Washington, D. C.

The effect of using isopropyl chloride as a solvent in place of ethyl ether in the official method was tried on various products with average results as shown in Table 2.

TABLE 2.
Results of ether extract determinations with different solvents.

Product	Isopropyl chloride	Ethyl ether
	per cent	*per cent*
Alfalfa	0.24	0.19
Corn meal	0.52	0.45
Cottonseed meal	7.90	7.83
Larro feed	3.63	3.70
Linseed meal	6.44	6.16

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 72.
[2] *J. Assoc. Official Agr. Chemists*, 1922, **6**: 61.

The results indicate that isopropyl chloride as an extraction reagent compares favorably with ethyl ether. It has advantages over ether in that it does not burn so rapidly and the fire risk is less.

A study was made of the effect upon ether extract determinations of grinding the samples finer. Different types of samples were tried by the official method using the Knorr apparatus. The results are shown in Table 3.

TABLE 3.

Results of ether extract determinations on different type samples.

	20 mesh	40 mesh	60 mesh
	per cent	*per cent*	*per cent*
Bran	4.70	4.79	4.90
Alfalfa	0.93	1.06	1.03
Corn meal	4.43	4.68	4.70
Cottonseed meal	7.83	7.93	7.92
Larro feed	3.71	3.83	3.93
Linseed meal	5.95	6.14	6.69

It would seem that the finer the sample is ground, up to the point where it is impracticable to grind it further, the more ether extract is obtained.

The collaborative work in this investigation was done by L. E. Bopst.

RECOMMENDATIONS.

It is recommended—

(1) That work on the comparison of the official method and the C. R. Smith method for ether extract determinations be continued next year.

(2) That a further study be made of the effect that grinding the sample finer will have upon the ether extract determinations.

REPORT ON CRUDE FIBER.

By G. S. FRAPS (Agricultural Experiment Station, College Station, Texas), *Associate Referee.*

The associate referee sent out samples of wheat bran, cottonseed meal and alfalfa meal to collaborators, with the request that they test these samples by three methods. Method No. 1 had a first reading for adoption as official in 1921; Method No. 2 requires boiling in a beaker and filtering through asbestos; and Method No. 3 should be the regular method used in the collaborator's laboratory. Later on, samples of linen cloth and cotton filtering cloth, which had been previously digested with equal parts of water and 1¼ per cent of caustic soda, were sent with the request that they be tested. The linen used is called butcher's linen or dress linen, about 50 threads to the inch, and the cotton filter-

ing cloth was furnished by G. L. Bidwell of the Bureau of Chemistry.

The referee received splendid cooperation, as is shown by this report. Especial mention should be made of the cooperation of G. L. Bidwell. The results of the analyses are shown in Table 1.

REMARKS OF COLLABORATORS.

A. L. Flenner, Maryland.—Method No. 3 differs from No. 2 in that the first filtration is made on linen instead of asbestos. The linen cloth is preferred when using suction and the cotton without suction. When the cotton cloth is used without suction on a 4-inch funnel, filtration is quick and the residue washes off easily.

C. S. Cathcart, New Jersey.—Method No. 1 suggested by the referee was not satisfactory. It was impossible to get satisfactory results and doubts are felt as to the outcome of this method.

N. C. Hamner, Dallas, Texas.—The usual laboratory method is much more convenient, quicker and less liable to error. There is too much frothing. It is difficult to keep the sample in the solution when the flask is used, as it is hard to shake the sample from the side of the flask. A tall 600 cc. beaker was used with a 500 cc. flask for condenser.

C. E. Shepard, Connecticut.—The laboratory method differs from the official in no essential particular except that boiling is not done under a water-cooled condenser. No trouble was experienced with Method No. 2 but the filtration was slow. The alkali digestion gave trouble on account of violent bumping, probably due to the large amount of asbestos present.

F. B. Porter, Fort Worth, Tex.—The laboratory uses a tall 600 cc. beaker covered with a 500 cc. flask filled with water. The proposed official method is inconvenient and unsatisfactory on account of frothing. With a reflux condenser attached to each flask, it is difficult to rotate the flask and keep sample in the solution.

J. J. Vollertson, Chicago.—The results by Method No. 2 varied more from the proposed official and the official method than they did from each other but this may be due to lack of practice in the method and not to anything fundamentally incorrect. The use of asbestos and a Büchner funnel is an advance over the linen filter in that the sample may be handled more easily and without loss. The use of Liebig condensers in the proposed official method requires a special set-up of apparatus and the results do not show an increased accuracy to justify it. The asbestos added in the proposed official method is of help in filtering through linen in case of such material as cottonseed meal. However, the amount used must be small to avoid filling the Gooch crucible too full. It is suggested that the proposed official method might be used for check or disputed samples. In case of an ordinary analysis, the substitute method would be better because of the superior ease of manipulation and the sufficient accuracy of the results. The method used in this laboratory is the old official method. The linen cloth is preferred as the sample can be more easily removed, but either cloth would be satisfactory.

L. D. Haigh, Missouri.—The 7.5 cm. Büchner funnel was found to be rather large, as it required so much asbestos. The large amount of asbestos from two filtrations taxed the capacity of the ignition crucible to hold it. A Büchner funnel, 6 cm. outside diameter, was used. This had smaller holes than the 7.5 cm. and required much less asbestos. Asbestos present with the feed in the boiling process seemed to increase the amount of bumping. In the laboratory method the liquid was heated in a tall 800 cc. lipless beaker covered with a flask filled with water, filtered both times on linen and transferred to a Gooch.

P. S. Tilson, Houston, Texas.—Methods 1 and 2 are not an improvement over the present official method. The sample of linen sent is admirably adapted to the purpose.

A. J. Patten, Michigan.—In the laboratory method (No. 3) an air condenser is used and both filtrations made on linen. The residue is then transferred to a Gooch.

J. L. St. John, Washington.—Our laboratory method follows the proposed official method; the second filtration is made on linen and then transferred to a Gooch.

W. G. Friedemann, Oklahoma.—No saving in time is effected by No. 2 and bumping was also observed. In Method No. 3 we used an 800 cc. lipless beaker.

W. F. Hand, Mississippi.—The cotton cloth works fairly well with ordinary feeds but it is very slow with cottonseed meal. The linen sent is thicker than the quality used in the laboratory and filters more slowly, but both give results closely in accord.

The following results were secured with the filtering medium sent:

	Cotton	Linen	Mississippi linen
	per cent	*per cent*	*per cent*
Molasses feed	10.15	10.31	10.27
Wheat shorts	4.66	4.71	4.71
Cottonseed meal	12.72	13.28	12.80

J. W. Kellogg, Pennsylvania.—The linen cloth is practically equal to the one used here. The cotton cloth filters much faster and gives very desirable results. The filtration of cottonseed meal and animal by-products is especially good.

B. J. Owen, Florida.—Both samples of cloth were used in official work for two months. The cotton cloth permits a more rapid filtration than the linen cloth because of its rougher texture and greater thickness, but the fiber clings to the cotton cloth to such an extent that it is difficult to separate the fiber from the cloth into the dish used for drying the fiber. The sample of linen filters much more slowly than the linen used in Florida.

J. B. Smith, Texas.—Method No. 2 is quicker and more convenient than Method No. 1. There seems to be no advantage in the use of asbestos with Method No. 1. The liquid filters quickly without it and there is less bumping. The work on Method No. 1 was done by the writer and that on No. 2 by Mrs. Graham, each determination on a different day.

R. F. Korfhage, Minnesota.—The laboratory method differs from the proposed official method in filtration on alundum crucibles, porosity R. A. 98, and washing with 1¼% sulfuric acid after the second filtration. An acid wash hastens the filtration of bone, tankage and meat scraps, which tend to clog the crucibles. Method No. 2 is very unsatisfactory because of the possibilities of loss of material although it does give higher results than the other methods. The cotton cloth sent is preferred as it filters more quickly.

H. D. Spears, Kentucky.—Amyl alcohol was used instead of air blast to prevent foaming. In the laboratory method the substance is added to the acid before it is heated; the first filtration is made on linen in a Hirsch funnel, the second on an alundum crucible, and the heating is performed in beakers. The beakers and flasks are more efficient than the Liebig condensers and certainly more practical. Addition of asbestos causes bumping. The sample of cotton is the most desirable filtering cloth used. On a sample of wheat feed, the laboratory method gave 7.50 and 7.45 per cent; filtering twice through alundum, 7.80 and 7.75 per cent.

J. D. Turner, Kentucky.—Comparisons of the cotton sent, the linen sent, and cloth regularly used were made on 12 regular feed samples. The results are given below. The two linens were about the same in texture and took the same length of time for filtration; the cotton was thicker and more porous and took less time for completing the work.

	Cotton	Linen	Kentucky linen
	per cent	*per cent*	*per cent*
Mixed feed	5.23	5.10	5.05
Mixed feed	7.73	7.85	7.88
Hog feed	4.98	4.93	4.85
Digester tankage	1.75	2.04	1.85
Poultry scratch	3.65	3.40	3.44
Poultry chick	2.80	2.70	2.85
Cottonseed feed	14.51	14.72	14.43
Cottonseed feed	16.83	16.93	16.79
Brewers dried grains	16.75	17.20	16.31
Middlings	5.30	5.55	4.48
Dairy feed	13.63	13.50	13.55
Laying mash	5.80	5.65	5.69

H. R. Baker, Wyoming.—This station is at the altitude of 7,200 feet, which affects the boiling point. To study this a 500 cc. Erlenmeyer flask, containing the liquid to be tested, was placed under a reflux condenser, just as in the crude fiber determination. A thermometer was lowered through the condenser until the bulb was immersed in the liquid, which was then heated to boiling.

The temperature of the sulfuric acid and caustic soda seemed to vary in proportion to the amount of water in the condenser at any one time.

When the liquid boiled at a constant rate as in the crude fiber determinations, the temperatures noted were as follows:

1.25% sulfuric acid varied between 97.5°C. and 98.0°C.;

1.25% sodium hydroxide varied between 96.5°C. and 97.0°C.;

Distilled water—no variation—temperature 96.0°C.

The boiling point of distilled water—determination in the usual manner by taking the temperature of the vapor arising from boiling water—was found to be 92.8°C.

The barometer reading when making these determinations was 23.285.

From these observations of the temperatures of the boiling solutions it would seem that the rate of boiling will have an effect on the results obtained in crude fiber work.

J. M. Bartlett, Maine.—The proposed official method does not meet with very much favor in this laboratory. The principal objection is the time that is required to carry out the filtrations with the large amount of asbestos that is proposed to use. Perhaps with more experience the method would meet with more favor but from the present amount of work done, it is not considered that the method is as accurate or convenient as the one now used. This consists in heating in a 500 cc. Erlenmeyer flask connected to a block tin condenser, filtering both times on linen and transferring to a Gooch.

G. L. Bidwell, Washington, D. C.—In your letter you ask for comments and suggestions. We are giving some of each with the hope that you will accept them in the spirit intended.

We were surprised to find a sample of alfalfa being used in this cooperative work, which was so coarsely ground. We have had difficulty in this laboratory securing checks on crude fiber upon straight alfalfa meal even when finely ground. This is due, no doubt, to the inability of the analyst to secure uniform charges, that is, charges containing the same amount of leaves and stems, for as you know stems run higher in fiber than leaves. Alfalfa ground to pass a 40-mesh sieve will give closer checks than the coarser material.

We have found the use of flasks for condensers to be unsatisfactory as well as inefficient; this was shown in our reports before the A. O. A. C. in 1920.

When asbestos was used as a filtering medium an additional transfer of the sample was necessary; also the charge became very bulky and would barely go into a Gooch crucible.

We do not see that the modifications suggested for trial improve the method, and the extra transfer certainly lengthens the time necessary for a determination.

DISCUSSION.

Table 1 contains the results reported by the individual laboratories. The average for each laboratory was used in making up the final averages. The proposed official method gives on an average slightly lower results than the method of filtration on asbestos. Eight of the 17 laboratories secured results within 0.3 per cent by the two methods applied to wheat bran, 10 on cottonseed meal and 2 on alfalfa meal.

The difference between the maximum and minimum is practically the same for the proposed official method and for the varied methods now used in the laboratories cooperating, when applied to wheat bran and cottonseed meal. The difference when filtering on asbestos is greater than that secured by the official method with wheat bran, but less with cottonseed meal. The difference between maximum and minimum averages with the proposed official method is 1.30 per cent for wheat bran, 2.05 per cent for cottonseed meal, and 3.97 per cent for alfalfa meal. The alfalfa meal was not ground fine enough. These differences are between the averages of the different laboratories, and not between the maximum and minimum of separate determinations.

Table 2 shows the distribution of the determinations with respect to the average for the proposed official method. The groups differ by 0.3 per cent, the average being approximately midway the median group. The distribution of the determinations is better for the proposed official method, especially with wheat bran, than for the other methods, but the distribution still leaves much to be desired. In other words, the agreement between the different laboratories is not so great as could be desired for a new official method, although it is better than, with the variety of methods now in use.

The writer is favorably disposed towards the proposed official method as he realizes that it is based upon a large amount of careful work by the previous referee. But the number of criticisms of the method and the wide variation in results secured from different laboratories prevent the writer from recommending this method for final adoption as official. While the proposed official method gives somewhat better results than the variety of methods in use in the different laboratories, these results leave much to be desired. It is possible that some of the differences will disappear with more familiarity with the method, and with the use of a uniform grade of filtering cloth. The method should appear so desirable to the various laboratories that they will be induced to adopt it in all essential details, for little advantage would be gained in adopting a method to be used by one or two laboratories.

TABLE

Results of cooperative

ANALYST	WHEAT BRAN		
	1-Proposed Official	2-Asbestos Filter	3-Laboratory Method
J. J. Vollertson, Morris & Co., Chicago	7.69 7.72	7.98	7.68 7.38
Average	7.71	7.98	7.53
A. P. Kerr, Louisiana	8.20	8.60	9.00
Claude R. Engle, Pennsylvania Department of Agriculture	8.07 8.40	8.66 8.33	7.72 7.65
Average	8.24	8.50	7.69
W. F. Hand, Mississippi	7.57	8.20	8.31
P. S. Tilson, Houston Laboratories, Houston, Texas	8.23	9.13	7.95
Percy O'Meara, Michigan	8.30 8.18	8.05 8.55	7.65 7.78
Average	8.23	8.30	7.72
J. L. St. John, Washington	8.10 7.97	8.75 8.68	7.64 7.86
Average	8.04	8.72	7.75
W. G. Friedemann, Oklahoma	8.62 8.85 9.05	8.75 8.67	8.77 8.93 8.55
Average	8.84	8.71	8.75
L. E. Bopst, Bureau of Chemistry, Washington, D. C.	8.57 8.50	8.69 8.52	
Average	8.53	8.60	
C. E. Shepard, Connecticut	7.91	8.22	7.97
F. W. Porter, Ft. Worth Laboratories, Ft. Worth, Texas	8.18	9.01	8.20
N. C. Hamner, Southwestern Laboratories, Dallas, Texas	8.05	8.98	8.05
L. H. Haigh, Missouri	7.97 7.79 8.41 8.42	8.46 8.57 8.74	7.73 7.58 7.97 7.95
Average	8.15	8.59	7.81
A. L. Flenner, Maryland	7.75	8.00	7.70
Average			
E. R. Tobey, Maine	8.33 8.15		7.89 7.81
Average	8.24		7.85

1.

work on crude fiber.

COTTONSEED MEAL			ALFALFA		
1-Proposed Official	2-Asbestos Filter	3-Laboratory Method	1-Proposed Official	2-Asbestos Filter	3-Laboratory Method
10.65	11.20	10.03	35.80	34.92	35.42
11.05		10.32	36.30		35.10
11.35	11.20	10.17	36.05	34.92	35.26
11.65	11.85	11.50	35.12	36.45	35.00
10.94	11.52	10.18	35.41	37.26	33.93
10.59	10.92	9.61	34.05	35.83	34.05
10.77	11.22	9.90	34.73	36.55	33.99
9.80	11.22	11.35	33.62	34.84	34.86
10.48	10.59	9.85	34.02	35.65	34.35
11.05	10.97	10.28	35.92	37.01	35.82
11.08	11.13	10.22	35.93	36.18	
11.07	11.05	10.25	35.92	36.80	35.82
11.40	11.64	10.44	33.94	37.04	34.90
11.20	12.05	10.50	33.28	37.47	35.14
11.30	11.86	10.47	33.61	37.25	35.02
11.77	11.41	11.67	38.40	37.17	37.79
11.55	11.50	11.80	37.10	38.90	37.95
11.35			37.25	38.60	
11.56	11.46	11.74	37.58	38.22	37.87
10.94	11.05		36.36	34.42	
11.26	11.07		37.90	36.37	
11.09	11.06		37.13	35.40	
10.59	10.70	10.46	34.56	35.32	36.13
10.79	10.79	10.30	34.66	35.25	35.48
10.62	11.21	11.14	34.80	34.97	34.25
10.72	11.18	10.29	36.56	37.56	35.26
10.85	11.22	9.94	35.73	34.69	34.53
11.40	12.24	10.42	37.02	37.50	36.90
11.63	11.87	11.22	37.56	39.45	
11.15	11.63	11.59	36.72	37.30	35.56
10.75	10.50	10.85	35.15	34.45	33.60
			35.45		33.50
			35.30		33.55
10.89		9.46	37.10		36.09
11.31		9.74	35.76		35.42
11.10		9.60	36.43		35.75

TABLE

Results of cooperative

ANALYST	WHEAT BRAN		
	1-Proposed Official	2-Asbestos Filter	3-Laboratory Method
Howell D. Spears, Kentucky	8.45 8.59	8.63 8.63	8.23 8.17
Average	8.52	8.63	8.20
Smith & Graham, Texas	8.69 8.76 8.72	8.71 8.64	
Average	8.72	8.68	
Roy F. Korfhage, Department of Agriculture, Minnesota	8.39 8.39	9.52 10.12 9.98 8.94	8.30 8.34
Average	8.27	9.64	8.32
Average (of averages)	8.19	8.61	8.05
Maximum (average)	8.87	9.69	9.60
Minimum (average)	7.57	7.98	7.69
Difference, maximum and minimum	1.30	1.71	1.31
Harold R. Baker, Assistant State Chemist, Wyoming*	9.70 9.80		8.59 8.61
G. Bitterman, Department of Agriculture, Wisconsin†	9.75 9.81 9.36	9.02 8.87 9.04	9.50 9.68 9.33
Average	9.64	8.97	9.50
W. G. Moore, Experiment Station,† Geneva, N. Y.	8.27 8.47	8.84 8.02	7.10 7.08
Average	8.37	8.43	7.09

*Owing to the high altitude these results are not included in the averages.
†Received too late to be included in the average.

The crude fiber method has been termed a definitive method by the previous referee, meaning that the results secured depend upon the exact details of the method used. If such is the case, the method should be defined in such a way as to be convenient and easy of manipulation. However, the results should not differ widely from the previous method, and this procedure should give agreeing results in the hands of different analysts. For example, there is no more reason for taking the method of boiling in a flask with a Liebig condenser as the standard, than for

1—*Continued.*
work on crude fiber.

COTTONSEED MEAL			ALFALFA		
1-Proposed official	2-Asbestos Filter	3-Laboratory Method	1-Proposed Official	2-Asbestos Filter	3-Laboratory Method
11.50	12.23	11.49	35.84	35.85	36.41
11.80	12.35	11.48	36.78	34.79	37.05
					38.91
					38.78
11.65	12.29	11.49	36.31	35.32	37.79
11.09	11.48		35.06	35.56	
11.10	11.52		35.37	35.74	
11.55			35.78	34.66	
11.25	11.50		35.46	35.32	
12.57	12.99	11.29	36.08	38.60	37.05
10.52	12.11	11.28	35.95	38.26	37.16
11.27	11.46	10.93	36.00	39.02	37.83
11.60	12.20		36.46	36.86	
11.49	12.19	11.17	36.30	38.18	37.35
11.02	11.31	10.74	35.46	36.03	35.50
11.85	12.29	11.74	37.58	38.22	37.87
9.80	10.50	9.60	33.61	34.45	33.55
2.05	1.79	2.14	3.97	3.77	4.32
13.31		10.61	39.67		39.23
13.06		10.88	39.45		38.25
12.40	11.84	10.59	36.10	36.60	36.62
12.01	11.76	10.50	38.22	38.22	36.45
12.65	12.33	10.68	36.91	36.91	37.00
12.35	11.97	10.59	37.24	37.24	36.69
10.66	10.90	9.55	35.32	32.88	33.48
10.72	11.52	9.58	35.04	36.82	33.50
10.69	11.21	9.56	35.18	34.85	33.49

taking the method of boiling in a beaker with a round condenser. One method might give slightly different results, but either method could be adopted as a standard. If more uniform results could be secured by one, or by the other method, it should be given the preference.

The assay flask mentioned in the method is no longer available, and reference to it should be omitted.

The cotton filtering cloth suggested by Bidwell seemed to be highly satisfactory, but the referee should not consider it good policy to pre-

TABLE

Deviation of averages from average by

GROUP	WHEAT BRAN		
	1-Proposed Official	2-Asbestos Filter	3-Laboratory Method
−1.66 −1.95	—	—	—
−1.38 −1.65	—	—	—
−1.06 −1.35	—	—	—
−0.75 −1.05	—	—	—
−0.46 −0.75	3	—	5
−0.30 −0.45	3	2	5
±0.15 Method No. 1	7	3	4
+0.30 +0.45	3	5	0
+0.46 +0.75	2	3	1
+0.75 +1.05	—	3	1
+1.06 +1.35	—	0	—
+1.36 +1.65	—	1	—
+1.66 +1.95	—	—	—
+1.96 +2.06	—	—	—
+2.06 +2.36	—	—	—
+2.36 +2.66	—	—	—

scribe a particular kind of cloth made by a particular manufacturer as the only kind of cloth to be used in an official method. There is no other way of describing such a filtering cloth.

At the meeting last year the associate referee on crude fiber was requested to incorporate the variation in the method necessary for prepared mustard. A recommendation has been made with this object in view.

L. E. Walter of the Wyoming station has called attention to the different results caused by high altitude. The lower boiling point of the liquid leaves a higher percentage of crude fiber. A note should be added to the method calling attention to this fact.

Bone meal comes under some feeding stuff laws, which require the guarantee of crude fiber in it, although it should contain practically no crude fiber, except from contamination. The present method gives from

2.

proposed official method.

COTTONSEED MEAL			ALFALFA		
1-Proposed Official	2-Asbestos Filter	3-Laboratory Method	1-Proposed Official	2-Asbestos Filter	3-Laboratory Method
—	—	—	2	—	1
—	—	1	1	—	1
1	—	2	0	—	2
0	1	2	2	1	0
1	1	3	2	3	2
4	3	1	2	1	2
4	1	1	1	5	2
3	4	1	0	1	2
5	3	4	2	0	1
—	2	—	3	1	0
—	2	—	1	2	0
—	—	—	0	0	0
—	—	—	1	1	1
—	—	—	1	0	0
—	—	—	—	1	2
—	—	—	—	1	—

4 to 6 per cent crude fiber, but if one-gram substance is used the amount of crude fiber is reduced to about 1 per cent. The quantity of sulfuric acid is probably not large enough to dissolve all the phosphate of lime from two grams. This matter is brought up for consideration without recommendation.

RECOMMENDATIONS.

It is recommended—

(1) That references to the assay flask be removed from Method No. 1, the proposed official method.

(2) That the paragraph concerning linen be changed as follows:

Filtering cloth should be of such character that while filtration is rapid no solid matter passes through. Either butcher's linen or dress linen with about 45 threads to the inch could be used, or No. 40 filtering cloth, made by the National Filter Cloth & Weaving Company, 57 Hope Street, Brooklyn, N. Y.

(3) That in accordance with the request of the committee on recommendations, the following description of the method for prepared mustard is offered for incorporation in the method when adopted. (It might be better to permit this variation to come in under the head of spices.)

In prepared mustard or similar pasty material, high in fat, proceed as follows:

Weigh 10 grams of the sample and transfer to a tall 8 ounce nursing bottle with 50 cc. of strong alcohol, stopper and shake vigorously. Add 40 cc. of ethyl ether, shake and let stand about 5 minutes with occasional shaking. Centrifuge and decant off the alcohol-ether mixture. Treat twice more with 40 cc. portions of ether, shaking, centrifuging and decanting as before. Rest the bottle on its side for a short time, without heat, to allow the ether to evaporate. Transfer the material with 1¼ sulfuric acid and determine crude fiber by the regular method.

If preferred, the sample may be treated with the alcohol and ether in a small beaker, finally transferred to a hardened 11 cm. filter paper and washed two or three times with ether.

(4) That the method be further studied with the view to its adoption on final reading as an official method. (This method was offered for first reading in 1921.)

G. L. Bidwell.—I am very much interested in the results obtained. I hope that those who are considering the method will take into consideration the one fact that no method will give as good results when first tried as it will later; in other words, when the analyst is more accustomed to using it.

Concerning the cotton cloth used for filtering, we saw the advertisement of it and wrote to the firm. We selected three samples of cloth from the collection sent and tested them. No. 40 was the one that seemed to suit the best. I realize the undesirability—if you want to use the word—of recommending any particular firm's cloth. However, we all realize the difficulty in getting a uniform cloth. In fact I do not remember that I have ever seen two lots of linen exactly alike. This cotton cloth is made for a specific purpose and is always uniform. Arrangements may be made whereby it can always be obtained and thus the problem of a uniform filtering medium may be solved.

On the question of condensers and boiling vessels, I do not think these have to be just as the original method specified. The beaker is just as good as the flask and any efficient condenser will do as well as the Liebig. Any changes along these lines will have our support. However, I should like to see the same types of apparatus specified for all laboratories, because this is the important point.

REPORT ON STOCK FEED ADULTERATION.

By H. E. GENSLER (Bureau of Chemistry, Department of Agriculture, Harrisburg, Pa.), *Associate Referee.*

The work on stock feed adulteration for this year includes a continued study of the method for the determination of hulls in rice bran as proposed by your former referee, B. H. Silberberg[1], and also of the method for the determination of grit in scratch feeds and bone in meat products formulated by your present referee[2]. As these methods were recommended for further study, samples were prepared and sent, with instructions, to 23 collaborators.

It was impossible to obtain rice bran which was absolutely free from hulls; however, that secured contained only a trace. This material was used as the basis for the samples in determining the amount of rice hulls present. The collaborators were advised to follow the Silberberg method, which requires the counting of hull particles in a 4 milligram portion of the sample, placed on a ruled slide and gently heated with chloral hydrate solution. Counts are made using samples which contain a known amount of hulls and, from the average number of particles observed per centum, a factor is obtained which is then used in computing the amount of hulls present in samples of unknown hull content.

Five samples of rice bran containing various amounts of rice hulls were sent to the collaborators for this work. Sample No. 1 was used as a basis for the other four samples; therefore the collaborators were instructed to obtain a count which should be used as a "blank" to be deducted from the counts obtained in subsequent determinations. Samples Nos. 2 and 3 were "standards" containing 10 per cent and 15 per cent of hulls, respectively; and Nos. 4 and 5 were "unknowns" and contained 8 per cent and 12 per cent, respectively. The collaborators were advised to familarize themselves with the appearance of rice hulls before making actual counts.

The results obtained are given in Table 1. It will be noted that while the counts obtained vary considerably, the reports upon the unknowns are in close agreement. The "blank" showed counts varying from 5 to 30 with an average count of 18 for the results of nine collaborators. The figures for Sample No. 2, containing 10 per cent of hulls, vary from 60 to 131, with an average of 98; and for Sample No. 3, containing 15 per cent of hulls, from 80 to 216, with an average of 150. In the case of the unknowns, counts ranging from 60 to 129 were reported for Sample No. 4, containing 8 per cent of hulls with an average of 87, and in the

[1] *J. Assoc. Official Agr. Chemists*, 1921, 5: 77.
[2] *Ibid.*, 1922, 5: 424.

case of No. 5, containing 12 per cent of hulls, the figures range from 64 to 167, with an average of 118.

The results reported for the percentage amount of hulls present are very close and in the case of Sample No. 4 are, with the exception of the report of Analyst No. 21, within 2.4 per cent of the amount known to be present. In the case of Sample No. 5, containing 12 per cent of hulls, percentages were reported ranging from 10 per cent to 14.1 per cent. All the results are within a range of 2.1 per cent. The average percentage of all the results on No. 4 is 9.3 and on No. 5, 11.6.

It is interesting to note the close results obtained by Analyst No. 12; notwithstanding that, in submitting his report, he stated that nothing more than an approximation could be made because the samples were manufactured from a bran which contained hulls as a contamination. The referee considers that unless a rather large amount of hulls was present in the sample used as a base, his suggestion of deducting the count obtained upon it from the other samples would only be in conformity with a practice often adopted in chemical work where correction factors are employed.

Probably the most striking feature of the averages is the fact that the ratio between the number of particles counted to the percentage of hulls present in each sample is as ten to one. One might assume, in other words, that every ten particles would represent the presence of 1 per cent of hulls.

It may fairly be concluded, from the figures obtained in this year's work as well as in the work previously done, that the method in question is very well adapted to the purpose intended and that the analyst can, with its use, ascertain quite accurately the amount of rice hulls present in a sample of rice bran. One or two rather wide variations from the actual amount of hulls present have been noted, but it is believed that these variations are the exception rather than the rule and should not be considered.

For the purpose of studying the method for the determination of grit in scratch feeds, devised by the referee, Samples Nos. 6 and 7, consisting of scratch feed and grit, were prepared. The results obtained in last year's work were unusually good for determinations of this character, but the question arose as to whether or not similar results would be obtained in an unground sample containing grit. One collaborator proposed the use of carbon tetrachloride. Accordingly, samples were prepared to prove the correctness of this suggestion. Sample No. 6 was an unground sample of scratch feed containing 10 per cent of grit. No. 7 consisted of a ground scratch feed to which was added 10 per cent of ground grit. It was the opinion of your referee that if results which approached 10 per cent could be obtained on both of these samples the method would be justified.

Table 2 is a condensed report of the results secured on these samples. Those obtained with the use of carbon tetrachloride check very closely the results obtained with the use of chloroform and demonstrate that either liquid can be used with equal advantage. Although variation of from 6.1 to 13.6 per cent existed in the analysis of Sample No. 6, the averages 9.4 per cent and 9.4 per cent correspond closely with the amount of grit present. The range is without a doubt due to the difference in the sample tested rather than in a failure of the method. This opinion is borne out in the reports on Sample No. 7 which had a definite content of grit. Most of the results are within a range of 0.5 per cent of the correct figures with no greater difference than 1.9 per cent. It is of interest to note that the averages for this sample are the same as those for No. 6. It might be well to recall at this time that eleven analysts working on samples prepared similarily to Sample No. 7, and containing 1, 3.5, 5 and 8.2 per cent of grit, respectively, obtained results which averaged 1.6, 3.6, 4.9 and 8 per cent for the respective samples.

It is evident that all the results secured on samples prepared to test this method justify its use in practical work.

The study of the application of the method for the determination of bone in meat products was arranged (1) further to test its accuracy; (2) to make a trial of the use of carbon tetrachloride as compared with chloroform; (3) to apply it to actual commercial samples; (4) to test its accuracy in estimating small amount of bone; and (5) to determine the analyst's ability to identify tankage in meat products.

Sample No. 8 consisted of 80 per cent of "cracklings" or "meat scrap" and 20 per cent of tankage. No. 9 consisted of No. 8 diluted with a high grade bone meal so as to contain exactly 10 per cent additional bone. The referee requested the collaborators to determine the amount of bone in both samples in order to estimate how nearly the difference of these two results would approach 10 per cent. Consultation of Table 3 will show that these figures were all very close to 10 per cent, only two out of eighteen showing any degree of variation. Averages of all results were 9.9 per cent and 10.2 per cent, using chloroform and carbon tetrachloride, respectively. Furthermore, it is of special interest to note that all analysts reported correctly the presence of tankage. Sample No. 10 was prepared to test the utility of the method in estimating small amounts of bone and contained only 2 per cent of bone. The results of work on this sample are also included in Table 3.

Collaborator No. 9 carried on experiments to determine whether any bone floated off with the supernatant liquid, by analyzing the "floats" for phosphoric acid and found its content to be "much higher than the phosphoric content of meat, blood or 'stick' ". Further, he reported that the proposed method was tried on steamed bone and the percentage of phosphoric acid in the floats was relatively high. He also called

attention to the fact that "sand, soil and cinders will sink and be weighed up with the bone". In reference to the first statement, it is not doubted that his results verify a condition wnich exists. However, the results just noted in the tabulation indicate that this loss is not serious. As indicated in the method, the residue is to be examined to insure its being bone. This clause will obviate any danger that contaminating ingredients will be included in the final results.

CONCLUSIONS.

The results on all samples are very gratifying. The percentages reported in the estimation of rice hulls indicate that a method has been found that is workable and dependable. The same thing is true in the determination of grit and bone. The use of carbon tetrachloride as an alternative liquid is approved and your referee has deemed it advisable to amend his method to include its use. He also has amended the method to include an examination of the residue of either bone or grit for the presence of impurities.

In the use of any micro-analytical method the operator must always bear in mind that if he can obtain a result which is a close approximation to correct content of ingredients, he has secured the most that can be expected from recourse to the use of such methods.

TABLE 1.

Determination of rice hulls in rice bran.

	COUNTS ON STANDARDS			COUNTS ON UNKNOWNS			
Analyst	Sample 1—Rice Bran (Blank)	Sample 2—10% Hulls	Sample 3—15% Hulls	Sample 4—8% Hulls		Sample 5—12% Hulls	
					per cent		*per cent*
2	17	91	137	63	7.0	114	12.5
5	11	79	120	68	8.5	95	11.9
8	12	101	153	87	8.6	106	10.5
10	5	80	108	74	10.4	93	11.6
12	27	128	216	112	8.5	167	12.0
14	..	131	204	129	9.6	135	10.1
16	24	119	203	119	10.0	191	14.1
17	20	80	110	60	8.0	100	13.0
19	30	110	165	80	7.3	110	10.0
21	15	60	80	80	15.0	64	10.7
Average....	18	98	150	87	9.3	118	11.6

The results obtained on all of the samples submitted to the collaborators fully justify the use and adoption of the methods employed.

TABLE 2.

Determination of grit in scratch feeds.

Analyst	SAMPLE 6–10% OF GRIT—UNGROUND: Chloroform	SAMPLE 6–10% OF GRIT—UNGROUND: Carbon Tetrachloride	SAMPLE 7–10% OF GRIT—GROUND: Chloroform	SAMPLE 7–10% OF GRIT—GROUND: Carbon Tetrachloride
	per cent	*per cent*	*per cent*	*per cent*
2	9.0	9.3	9.7	9.8
5	9.9	9.7	9.6	9.1
8	13.5	13.6	9.4	9.4
9	6.1		8.8	
10	10.6	10.4	9.6	9.1
11	8.1	7.8	9.3	8.1
14			9.8	9.6
16	11.2		9.4	
17	7.4	6.7	8.9	10.3
19	9.0	8.5	10.4	9.8
21	9.1	8.8	9.2	9.3
Average...	9.4	9.4	9.5	9.4

TABLE 3.

Determination of bone in meat products.

	SAMPLE 8—UNKNOWN AMOUNT OF BONE—TANKAGE PRESENT			SAMPLE 9—NO. 8 WITH 10% BONE ADDED			SAMPLES 8 AND 9—DIFFERENCE 10%		SAMPLE 10—MEAT MEAL—BONE 2%		
	Bone			Bone			Estimated Difference		Bone		
Analyst	Chloroform	Carbon Tetrachloride	Tankage	Chloroform	Carbon Tetrachloride	Tankage	Chloroform	Carbon Tetrachloride	Chloroform	Carbon Tetrachloride	Tankage
	per cent	*per cent*		*per cent*	*per cent*		*per cent*	*per cent*	*per cent*	*per cent*	
2	42.2	42.0	Present	48.5	48.8	Present	10.5	11.0	2.2	1.9	Trace
5	42.1	40.5	Present	47.4	46.8	Present	9.5	10.4	2.1	2.1	None
6	41.2	40.4	....	47.2	46.9	....	10.1	10.5	2.1	2.1	....
9	38.1	.....	....	46.1	.....	....	11.8	.....	2.1	.....	....
10	38.6	37.8	Present	44.3	43.5	Present	9.6	9.5	3.9	3.8	None
11	42.9	40.2	Present	49.1	46.3	Present	10.5	10.1	2.4	2.0	None
14	42.0	.....	....	46.4	46.3	Present	8.6	....	2.2	2.1	None
16	39.9	.....	....	45.3	.....	....	9.4	....	2.0	.....	....
17	43.4	41.6	....	49.4	48.5	....	10.3	11.1	2.4	1.9	....
19	41.5	41.0	Present	46.6	45.6	Present	9.3	8.7	2.3	2.1	None
21	41.2	39.9	Present	46.9	46.5	Present	9.8	10.6	1.9	1.9	None
Avge...	41.2	40.4		47.0	46.6		9.9	10.2	2.3	2.2	

RECOMMENDATIONS.

It is recommended—

(1) That the method for the determination of rice hulls in rice bran as devised by B. H. Silberberg be adopted by this association as a tentative method.

(2) That the method for the determination of grit in scratch feeds and bone in meat products as devised by H. E. Gensler be adopted as a tentative method.

(3) That the incoming referee proceed along the lines already followed, either presenting some method for the micro-analytical quantitative determination of ingredients or perhaps applying the methods just proposed for the determination of different ingredients, such as cottonseed hulls in cottonseed meal or oat hulls in oat feed.

THE DETERMINATION OF STARCH CONTENT IN THE PRESENCE OF INTERFERING POLYSACCHARIDES, AS IN IMPURE LINSEED PRODUCTS[1].

By G. P. Walton and M. R. Coe (Bureau of Chemistry, Washington, D. C.).

As indicated by the title, this study had its origin in an investigation of the production and handling of linseed by-products. The seed of the flax plant contains no starch. Therefore, any starch found in a linseed meal or cake is non-flax material and, in a general way, it may be considered a rough measure of the foreign matter present. Owing to the presence of important quantities of mucilage, it was found to be impossible to determine the starch content of linseed cake or meal by the official starch methods[2]. The linseed mucilage seriously interferes in two ways: (1) Moistened with water or weak alcohol it forms an impervious mixture which prevents the leaching out of sugars by these solvents and makes impossible the preliminary extraction required by the official methods; (2) the mucilage, itself a polysaccharide, yields dextrose on hydrolysis and hence must be eliminated before the acid hydrolysis, or the figures obtained for starch will be erroneously increased.

The important facts brought out by the investigation are: (1) It is possible to extract the sample of linseed meal with 35 per cent alcohol for the elimination of sugars; (2) it was found that the mucilage could be coagulated and precipitated by 60 per cent alcohol and eliminated

[1] Abstract only; the complete paper will be published in the Journal of Agricultural Research.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 95.

by means of filtration; and (3) it was definitely established that the starch conversion products obtained by properly conducted malt diastase digestion remain in solution in 60 per cent alcohol.

In using the method, painstaking attention should be given to details, more particularly to those dealing with the colloidal substances involved. Such are the operations of gelatinizing to a smooth paste and the thorough discomposing of coagula and subsequent mixing. It is also highly important to control the conditions that prevail during the dissolving and conversion of the starch. It has been demonstrated in the Bureau of Chemistry that the starch is best brought into solution by starting the first digestion with malt infusion at a temperature well below 55°, then slowly raising to 70°, and after maintaining this temperature for the specified time, continuing to increase the temperature to 80°. While the sugar-forming enzymes, *e. g.*, the maltase, are believed to be destroyed by temperatures of 70° and above, other starch liquefying enzymes present in the malt infusion are more active at the higher temperatures, and complete solution of the starch is attained. The second saccharifying digestion is conducted at 55°.

Owing to the care that must be exercised in its use, the method of analysis is described in far more detail than ordinarily would be justifiable.

The method follows:

Method for the Determination of the Content of Starch in the Presence of Interfering Polysaccharides.

PREPARATION OF MALT EXTRACT.

Select clean, new barley malt of known efficacy, and grind only as needed. Grind the malt well, but not so fine as greatly to retard filtration. Prepare an infusion of the freshly ground malt immediately before it is to be used. For every 80 cc. of the malt extract that will be required, digest 5 grams of the ground malt with 100 cc. of distilled water, at room temperature, for 2 hours. (The time of digestion may be shortened by use of an electric mixer. If the malt and water mixture is stirred by the machine for periods of 5 minutes, 3 or 4 times in the course of an hour, the extraction should be sufficiently complete.) Filter to obtain a clear extract. (It may be necessary to return the first portions of the filtrate to the filter.) Mix the infusion well.

DETERMINATION.

(*a*) *Preparation and extraction of the charge.*

Grind the material to a very fine powder and mix well. (The entire sample should be ground to pass freely through a sieve of not less than 40 mesh to the inch, and it is preferable that it be fine enough to pass a 60-mesh sieve.)

Weigh out a definite charge of from 2 to 6 grams of the finely pulverized sample, using the smaller charges in the case of materials containing much gel-forming substance. (Charges of 4 grams for linseed meal, or 3 grams for dried apple pomace, have been found to be satisfactory.) The weight of starch in the charge should not exceed 1.5

grams. Transfer to a dry filter paper held in place in a glass funnel of the usual type[1]. It is not necessary to use a hardened filter; any tight, high-grade paper, 12½ or 15 cms. in diameter will be found satisfactory.

Extract the charge with 5 successive portions of ethyl ether, using more than enough to cover the charge. Use a cover glass to retard evaporation. After completing the extraction, allow the ether to evaporate and extract with weak alcohol. The concentration of the alcohol may be varied to suit the material under examination. In the case of linseed meal it is necessary to use 35% alcohol (by volume), while for dried apple pomace 25% served best. Use 300 cc. of the alcohol to obtain the required thoroughness of extraction. Follow this with several filterfuls of 95% alcohol and finish the leaching operations with a second ether extraction. (It is desirable at this point to allow the charge to stand overnight so that the ether and alcohol may evaporate, since alcohol must be eliminated before starting the digestion with malt.)

At this stage start the preparation of the malt infusion.

A correction for the dextrose in the malt extract is obtained by conducting a control determination (preferably in duplicate). Starting with a piece of the filter paper extracted with alcohol, add distilled water and carry out the control side by side with the actual starch determination, subjecting it to the gelatinization temperature, adding the same quantities of malt extract, and treating it similarly in every respect.

(*b*) *Gelatinization.*

To return to the primary determination, transfer the paper and charge (practically freed from the alcohol) to a 300 cc. Erlenmeyer flask, and mix well with from 20 to 30 cc. of distilled water—macerating paper and material so as to obtain a perfectly smooth paste. Add 100 to 120 cc. of boiling water; mix quickly but thoroughly and, with constant stirring, heat the contents of the flask until boiling freely. (In the case of mucilaginous materials like linseed meal it is necessary to transfer the flask to a boiling water bath to complete the gelatinization without scorching.) Gelatinize thoroughly without scorching or adhesion of material to the bottom of the flask. The mixture should be smooth and free from lumps.

(*c*) *Malt-diastase digestion.*

Cool to 50° or below, add 20 cc. of the malt infusion to controls as well as charges, and place the flasks in a temperature-controlled water bath. Keeping the "mash" thoroughly mixed, gradually raise the temperature to 70°, taking from 20 to 30 minutes. Maintain at 70° for 30 minutes, stirring the mixture from time to time; then increase the temperature to 80° and maintain for ten minutes. Finally heat to the boiling point. Keep the mixtures well stirred as this is equivalent to a second gelatinization.

Cool the contents of the flasks, and the water bath as well, to 55°. Add 20 cc. of the malt extract, mix well, and maintain at 55° for 1 hour, stirring about once every 10 minutes. At the termination of the digestion rapidly increase the temperature to above 80°.

(*d*) *Defecation with 60% alcohol.*

The total volume of the hot "mash" should not exceed 200 cc. Transfer each "mash" to a 500 cc. volumetric flask. (A little hot water may be used for rinsing provided the total volume of the mixture does not exceed 200 cc. Reserve the flask for subsequent rinsing.) Measure out 316 cc. of 95% alcohol and add this, a little at a time, to the contents of the flask, with thorough shaking after each addition. As soon as enough alcohol has been added to coagulate colloidal matter, allow the coagulum to settle somewhat, and pour a little of the supernatant liquid back into the Erlenmeyer flask used in the digestion, thoroughly rinsing the contents into the volumetric flask. Com-

[1] An ordinary paper clip serves well to clamp the paper in place.

plete the addition of the 316 cc. of strong alcohol with constant mixing, avoiding any loss of material and, after cooling to room temperature, adjust the volume with water so that the quantity of *liquid* is 500 cc., *i. e.*, allow for the volume occupied by the solid material by adding 3 cc. of water for every 4 grams of charge present, after bringing the contents of the flask up to the 500 cc. mark.

At this stage of the procedure the starch conversion products from the original charge should be contained in the 500 cc. of 60% alcohol. (The determination may be interrupted at this stage for several days, but the volume of solution would have to be readjusted if a change in temperature occurred.)

Mix thoroughly, breaking up any ropy coagulum as much as possible by pouring back and forth from one large beaker to another. Filter through dry paper. (Test the solid residue for starch, either microscopically or by the iodine color test after elimination of alcohol and gelatinization with water. If more than the merest trace of starch is found, reject the entire determination.) Evaporate exactly 200 cc. of the filtrate on a steam bath to a volume of from 15–20 cc., or until practically all alcohol has been expelled. Do not allow the evaporation to proceed to dryness.

(e) Acid Hydrolysis.

Transfer the aqueous residue of starch conversion products to a 200 cc. volumetric flask with hot water, using a rubber policeman to recover all the dextrine. Allow to cool somewhat and complete the volume to 200 cc. Transfer the entire contents to a suitable digestion flask; add 20 cc. of hydrochloric acid (sp. gr. 1.125) and connect with a reflux condenser. Heat in a boiling water bath for 2½ hours.

(f) Purification of the dextrose solution and determination of dextrose by copper reduction.

Cool, and in the case of linseed meal or other material yielding solutions which at this stage need further purification, add not more than 1 cc. of a 10% solution of phosphotungstic acid in 1% hydrochloric acid. Mix, and allow to stand at least 15 minutes. Increase the volume with water to 250 cc. in a volumetric flask; mix well and filter through dry paper. Take 200 cc. of the filtrate and, while stirring, partially neutralize by adding 10 cc. of a heavy solution of caustic soda (44 grams of sodium hydroxide per 100 cc. of the cooled solution) and then nearly complete the neutralization with a little powdered sodium carbonate. (The anhydrous carbonate will be found preferable, as it dissolves rapidly.) Transfer to a 250 cc. flask with water, cool to room temperature, make up to mark, and mix well. Filter, if necessary, and determine the dextrose in a 50 cc. aliquot of the filtrate by copper reduction, employing the gravimetric method of either Munson and Walker[1], or Allihn[2]. Correct the weight of dextrose obtained by the weight of dextrose[3] found for the same aliquot of the malt control and multiply the corrected weight of dextrose by 0.90 to obtain the weight of starch. (This factor 0.90 represents the theoretical ratio between starch and dextrose and was used throughout this study; but it has been shown by a number of investigators[4] that the factor 0.93 more nearly represents the actual yield.)

Aliquots:

$$\text{Charge} \times \frac{200}{500} \times \frac{200}{250} \times \frac{50}{250} \text{ or,}$$

$$\text{Charge} \times 0.064.$$

[1] *J. Assoc. Official Agr. Chemists, Methods*, 1920, 78.
[2] *Ibid.*, 90.
[3] In the *Diastase Method, Assoc. Official Agr. Chemists, Methods*, 1920, 96, the direction to "correct the weight of reduced copper" by that found in the malt blank is erroneous.
[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 95.

SUMMARY OF RESULTS.

The following results have been obtained by this method:

For a traced linseed cake known to contain approximately 3.3 per cent of nonflax matter, 1.34 per cent of starch was found; for a sample of prepared starch containing 87.5 per cent of starch there was found 87.2 per cent, a recovery of 99.6 per cent; and with 3.8 grams of the linseed cake and 0.2 gram of the prepared starch, having a theoretical starch content of 5.65 per cent, there was found 5.5 per cent, a recovery of 97.2 per cent. With 3.5 grams of the linseed cake and 0.5 gram of the starch (theoretical starch content 12.11 per cent), there was found 11.9 per cent of starch, a recovery of 98 per cent; and for a charge of 3 grams of linseed cake and 1 gram of the starch (theoretical starch content 22.88 per cent), there was found 22.85 per cent of starch, a recovery of 99.9 per cent.

The results obtained on a few samples of dried apple by-products indicate that the method may be applied equally well to substances containing important quantities of pectin, such as dried apples and dried apple pomace.

READING THE FAT COLUMN IN THE BABCOCK TEST FOR MILK.

By C. F. Hoyt (Dairy Laboratory, Department of Agriculture, Sacramento, Calif.).

The Babcock test for the estimation of butter fat in whole milk has assumed a position of great importance in the dairy industry of this country and because of its simplicity, ease of operation and cheapness it fills an uncontested place. Since the test is not based on exact analytical methods, as is necessary for the separation and weighing of a pure chemical substance, the conception concerning it from the beginning has been that the details of operation should give results equivalent to those obtained by more rigorous analytical methods. Therefore, specifications for the graduation of test bottles, speed of tester, time of centrifuging, temperature of reading and manner of reading the meniscus must be made.

The dairy industry of the country is indebted to S. M. Babcock of the University of Wisconsin for this test. He gave a description of his new centrifugal method in 1890[1] and again in 1892[2]. He checked the method against the gravimetric asbestos method on 30 samples of whole milk and found practically exact agreement between average values. The maximum positive deviation from the gravimetric was 0.3 per cent and the maximum negative deviation was 0.2 per cent.

---

[1] Univ. of Wisconsin Agr. Expt. Sta. Bull. 24.
[2] *Ibid.*, 31.

REVIEW OF LITERATURE.

In the years immediately following the publication of the test various investigators made comparisons of values obtained by it with those obtained by other methods. The Connecticut Agricultural Experiment Station[1], in 1891, reported comparisons between the "standard method used in chemical laboratories" and the Babcock method which showed an average difference of 0.01 per cent on 32 samples. The greatest difference in any individual case was 0.18 per cent. In six cases the difference exceeded 0.1 per cent; in 18 cases it was less than 0.05 per cent; and in 17 cases the "standard method" gave lower, and in 15 cases higher results than did the Babcock. No details were given as to the "standard method" used and very few on the Babcock.

B. H. Hite[2], in 1890, reported comparisons of the Babcock method with several other similar methods and with the Adams method. Three analyses of whole milk were given in which both the Babcock and the Adams methods were used. The original instructions given by Babcock were followed and the same type of centrifuge was used. It was stated that difficulty was encountered in obtaining fat free from casein and that the results differed widely from those obtained by the Adams method.

E. H. Farrington[3], in 1891, reported comparisons of the Babcock method with those of Patrick and Beimling and with the sand, asbestos and Adams extraction methods on 12 samples of milk and found close agreement. The details of operation were not given but it is to be presumed that Farrington followed in general the original instructions of Babcock and used the same type of apparatus.

Harry Snyder[4], in 1891, reported comparisons between the Babcock method and the gravimetric asbestos method on 28 samples of milk. He obtained close agreement but did not give details of operation.

John Sebelien and Kristoffer Stören[5], in 1894, reported comparisons of the Babcock and Adams methods on 35 samples. They apparently departed somewhat from the directions of Babcock and stated that they read the tests from "hot" water. They obtained closely agreeing results.

It would appear that little work has been done on the method in recent years—that is since modifications have been made in the centrifuge and more rigid standards for manipulation have been established. It is true that Julius Hortvet[6], in 1917, reported the results of collaborative work on milk done by 10 different men, showing comparisons of

[1] Annual Report, Connecticut Agr. Expt. Sta., 1891.
[2] 3rd Annual Report, West Virginia Agr. Expt. Sta.
[3] Univ. of Illinois Agr. Expt. Sta. Bull. 14.
[4] Cornell Univ. Agr. Expt. Sta. Bull. 29.
[5] *Chem. Z.*, 1894, 18: 1816.
[6] *J. Assoc. Official Agr. Chemists*, 1917, 2: 238.

results obtained with the Babcock method with those obtained by the Roese-Gottlieb and some other methods. The different collaborators were instructed to carry out the method "according to procedure commonly recognized as correct" and to use an 8 per cent bottle. The results reported were obtained by averaging the readings to the top and to the bottom of the upper meniscus. Although one or two of the collaborators obtained results widely at variance with those obtained by the Roese-Gottlieb method, an average of the results by the Babcock method read as indicated was 0.04 per cent lower than the average of the results obtained by the Roese-Gottlieb method.

D. E. Bailey[1] also reported, in 1919, a study of the Babcock test for butterfat in milk, giving the results of 190 comparisons involving 1,476 tests where both the Babcock method and the gravimetric method were used. The average of all Babcock readings made by one individual was 0.076 per cent higher than the average of all gravimetric determinations. When readings of the same tests by several individuals were made the average became 0.060 per cent higher than the gravimetric determinations. Many data were presented concerning the effect of different factors on the appearance and the reading of the test.

With more extended use of the test in various fields, especially for the purpose of providing a basis of payment for milk, the matter of controlling the various details of its operation so as to secure uniform and accurate results has been assuming increased importance. In California the advantage of a close adherence to uniform practice in relation to these details has been recognized to the extent that an elaborate set of rules to cover the matter has been enacted into law. These rules provide exact specifications as to the construction and accuracy of graduation of glassware, the speed of the centrifuge, the temperature of reading, the point on the meniscus to which the reading is to be made and the keeping of records. Moreover, operators of the test are subject to examination and licensing.

It is evident, however, from a reading of the original publications and from several specific facts that Babcock did not contemplate a degree of accuracy such as that required today. For example, bottles graduated to only 0.2 per cent instead of to 0.1 per cent were used; a variation in accuracy of graduation of the test bottle of as much as 0.3 per cent in the whole length of the scale was permitted; the bottles were whirled five minutes, filled to the 7 per cent mark and whirled one minute; and the reading was made at any temperature between 110°F. and 150°F. No readings were made to less than 0.1 per cent.

Changes in the form of apparatus used and in some of the details of conducting the test have been made since the original work on the

[1] *J. Dairy Science*, 1919, 2: 331.

method was done and since the various investigators reported the results of their findings. The first centrifugal machines used were those in which the bottles were inclined at an angle of about 30 degrees from the horizontal and they were turned by hand or driven by a belt. The machines in common use today are driven by a steam turbine or by electricity, and the bottles lie in a horizontal position during the whirling. The bottle required by law in California is the 8 per cent bottle graduated to 0.1 per cent instead of the 10 per cent bottle graduated to 0.2 per cent, which was originally used. The standard of graduation requires that 13.5471 grams of clean, dry mercury shall fill the space equivalent to 5 per cent, instead of 13.59 grams as originally specified. It is definitely known that one of the principal makers of glassware in the country has until recent years used a standard of graduation at variance with that used at present; moreover it is reasonable to suppose that the glassware made now is much more uniform and accurate than it was formerly. A time of whirling somewhat different from the original is set in the standard method[1] for conducting the test, and the temperature of reading is more definitely fixed.

SCOPE OF INVESTIGATION.

In view of the changes made in the apparatus and in the directions for conducting the test, a further study of the percentages obtained by the Babcock method as compared with those obtained by other methods is demanded. In fact, serious question has been raised as to the complete accuracy of the test using the present apparatus and specifications for manipulation. The work reported in this paper was undertaken in order to obtain information on the effect of one of these specifications, namely, that requiring the reading of the fat column from the bottom of the lower meniscus to the top of the upper meniscus.

Samples of milk were obtained, some composite and others from the complete milking of individual cows; all were fresh and in perfect condition. No sample was used which showed any indication of churning or on which the cream had risen sufficiently to become hardened. The percentage of fat was obtained by the following methods: Babcock; Roese-Gottlieb, run on the Mojonnier apparatus; Adams paper coil; and asbestos gravimetric.

The writer wishes to acknowledge encouragement and advice given him throughout the investigation by George P. Gray, Chief of the Division of Chemistry. He is also indebted to N. C. Smith, R. W. Newman and M. B. Kennedy for making some of the tests and assisting in a review of the literature and in the preparation of the manuscript.

---

[1] Method of the American Dairy Science Association, *J. Dairy Science*, 1922, 5: 178; it is also true of the method of the Association of Official Agricultural Chemists, *Assoc. Official Agr. Chemists, Methods*, 1920, 228.

METHODS.

Babcock method.

The milk test bottles used were the 18-gram, 6-inch, 8% bottles graduated to 0.1%. They conformed to the specifications of the Association of Official Agricultural Chemists[1]. These specifications are as follows: "The total per cent graduation shall be 8. The total height of the bottle shall be 150–165 mm. (5⅞–6½ inches). The capacity of the bulb up to the junction with the neck shall be not less than 45 cc. The graduated portion of the neck shall have a length of not less than 63.5 mm. (2½ inches) and the neck shall be cylindrical for at least 9 mm. below the lowest and above the highest graduation marks. The graduations shall represent whole per cents, halves and tenths of a per cent". Each bottle was found to be completely accurate for the interval between the 0 and the 4% line and for the interval between the 4% and the 8% line. The examination for accuracy was made by the official method of the Association of Official Agricultural Chemists. The bottle was filled with mercury to the 0 line, and 10.8377 grams of clean, dry mercury for the interval between 0 and 4% and the interval between 4% and 8% were weighed on an accurate balance The reading at the line was observed by a glass having a low magnification.

The pipets used conformed to the specification of the Association of Official Agricultural Chemists and to the more detailed specifications of the Bureau of Standards[2] These specifications are as follows:

	Millimeters
Total length of pipet not more than	330
Outside diameter of suction tube	6–8
Length of suction tube	130
Outside diameter of delivery tube	4.5–5.5
Length of delivery tube	100–120
Distance of graduation mark above bulb	30–60
Tolerance—0.05 millileters.	
Nozzle straight.	
Delivery 17.6 millileters of water at 20°C. in 5 to 8 seconds.	

The delivery was well within the tolerance, the variations from exact accuracy in millileters, being as follows: +0.01, +0.02, +0.03, +0.04. Nearly all the measurements were made with pipets having a delivery which varied from exact accuracy by +0.03 or less.

The testing was conducted according to the specifications and directions of the American Dairy Science Association[3] except that chemically pure sulfuric acid, specific gravity 1.82–1.83, instead of the commercial variety was used. The tester was of the 24-bottle, steam-turbine, Facile type made by D. H. Burrell & Co. The diameter of the wheel was 20 inches. The speed was held as nearly as possible to 760 revolutions per minute.

The milk was pipetted into the test bottles, and the weights were obtained and recorded. Acid was added (both milk and acid being at a temperature between 60° and 70°F.), and the milk and acid were mixed. The bottles were whirled for 5-, 2- and 1-minute periods, respectively, sufficient distilled water at a temperature of about 200°F. being added after the first whirling to fill the bottle to the bottom of the neck, and after the second whirling to near the top graduation. The temperatures during whirling were approximately as follows:

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 227.
[2] U. S. Bur. Standards Circ. 9: 7th ed.
[3] *J. Dairy Science*, 1922, 5: 175.

	°F.
Beginning first period	115
End first period	124
Beginning second period	163
End second period	140
Beginning third period	165
End third period	142

The test bottles were placed in a water bath, maintained at a temperature of 135° to 140°F., for at least 10 minutes before reading. Readings were made with a pair of dividers, first from the bottom of the lower meniscus to the top of the upper meniscus and then from the bottom of the lower meniscus to the line of separation between the fat column and an overlying layer of glymol. All readings were made by two or by three men, and the average of these readings is reported. No reading was made on a fat which was not perfectly clear and free from charred and white substances.

Roese-Gottlieb (Mojonnier) method.

The Roese-Gottlieb is an official method of the Association of Official Agricultural Chemists. It was run on the Mojonnier apparatus. A pipet holding 10 grams of milk was weighed on an analytical balance, the milk transferred to the extraction flask and the empty pipet weighed. The reagents were added in the following order: 1.5 cc. of ammonia; 10 cc. of 95% alcohol; 25 cc. of ethyl ether; 25 cc. of petroleum ether. Thorough shaking followed the addition of each reagent, the flasks being closed with cork stoppers which had been extracted with ether. The ether solution was separated from the other liquid by centrifuging for about a minute. The ether solution was poured into dried and weighed aluminum dishes and the extraction repeated twice, using 15 cc. of each of the ethers for these extractions, making 3 extractions in all. The ether was evaporated from the dishes on a hot plate, and the fat was dried on a hot plate in an oven at 135°C. for 5 minutes, under 29 inches of vacuum. The dishes were cooled in a desiccator and weighed. Blank determinations were made using the same flasks, reagents and cork stoppers, and the results were corrected by the blank obtained.

Adams paper coil method.

Schleicher and Schüll fat-free paper was used. A pipet containing 5 grams of milk was weighed; the milk was spread over the paper in such a way that the borders were not wet by the milk and the empty pipet weighed. The paper was then set on edge and left at slightly above room temperature until nearly dry. It was then rolled up and dried in a water oven to constant weight, after which it was transferred to a Soxhlet apparatus and extracted for a length of time equivalent to at least 4 hours when the ether syphons over from the extraction tube 10 times per hour. When the syphoning proceeded at a lower rate than this the time of extraction was prolonged accordingly.

Ethyl ether was used for extraction. This was first washed repeatedly with distilled water and then allowed to stand several days, first over sticks of sodium hydroxide and then over metallic sodium. The flasks were nearly freed from ether on a hot plate and finally dried to constant weight in a water oven. Blank determinations were made using the same fat-free paper, ether and time of extraction. Results were corrected by the blank obtained.

Asbestos gravimetric method.

About 2 grams of freshly ignited woolly asbestos were placed in a previously ignited, coarse, alundum thimble, to which about 5 grams of milk, weighed from a pipet as in the Adams method, was transferred. It was dried to constant weight in a water oven and transferred to a Soxhlet apparatus with small wads of dried absorbent cotton placed over the asbestos and in front of the syphoning tube. The ether, time of extraction and drying were the same as in the Adams method. Blanks were made and results corrected accordingly.

RESULTS.

Table 1 shows the results found by the Babcock and the Roese-Gottlieb (Mojonnier) methods. The averages of the percentages found are as follows: Babcock, reading to top of meniscus, 4.204; Babcock, reading with glymol, 4.063; Roese-Gottlieb (Mojonnier), 4.088. Table 2 shows the results found on those samples run not only by the Babcock and Roese-Gottlieb (Mojonnier) methods but also by the Adams and asbestos methods. The average percentages are as follows: Babcock, reading to top of meniscus, 4.129; Babcock, reading with glymol, 3.992; Roese-Gottlieb (Mojonnier), 4.050; Adams, 4.038; asbestos, 3.956. Table 3 shows the variations in percentages found by the Babcock method from those found by the Roese-Gottlieb (Mojonnier) method. The plus sign indicates that the percentages by the Babcock method are higher and the minus sign, that they are lower than the percentages found by the Roese-Gottlieb (Mojonnier) method. The averages of the readings to the top of the meniscus are 0.116 above, and of those with glymol 0.025 below, the Roese-Gottlieb (Mojonnier) figures. Table 4 shows the variations found on those samples run not only by the Babcock and Roese-Gottlieb (Mojonnier) methods but also by the Adams and asbestos methods. The average of the readings to the top of the meniscus is 0.079 above the Roese-Gottlieb (Mojonnier) figures, 0.091 above the Adams and 0.173 above the asbestos; the average of the readings with glymol is 0.058 below the Roese-Gottlieb (Mojonnier) figures, 0.046 below the Adams and 0.036 above the asbestos

TABLE 1.

Percentages of fat found in milk by the Babcock and the Roese-Gottlieb (Mojonnier) methods.

SAMPLE NO.	GRAMS TAKEN		BABCOCK—READING TO TOP OF MENISCUS			READING WITH GLYMOL			ROESE-GOTTLIEB (MOJONNIER)		
	A	B	A	B	Average	A	B	Average	A	B	Average
1	18.04	18.00	3.64	3.55	3.595	3.50	3.39	3.445	3.52	3.52	3.520
2	18.00	18.00	3.84	3.84	3.840	3.70	3.64	3.670	3.69	3.66	3.675
3	17.98	.....	4.71	4.69	4.700	4.57	4.60	4.585	3.56	4.52	4.540
4	.....	.....	3.60	3.59	3.595	3.43	3.43	3.430	3.43	3.45	3.440
5	18.04	.....	3.38	3.40	3.390	3.23	3.26	3.245	3.25	3.24	3.245
6	.....	.....	3.39	3.36	3.375	3.23	3.22	3.225	3.26	3.22	3.240
12	18.04	18.01	5.00	5.02	5.010	4.87	4.86	4.865	4.90	4.94	4.920
15	18.00	18.01	3.42	3.42	3.420	3.32	3.31	3.315	3.26	3.28	3.270
16	18.12	18.01	3.81	3.79	3.800	3.67	3.66	3.665	3.69	3.66	3.675
17	18.00	18.01	4.14	4.14	4.140	4.05	4.04	4.045	4.05	4.06	4.055
19	17.97	17.97	5.11	5.11	5.110	4.99	4.98	4.985	4.94	4.96	4.950
20	17.96	17.97	7.12	7.11	7.115	6.98	6.93	6.955	7.03	7.05	7.040
21	18.01	18.06	4.41	4.42	4.415	4.30	4.33	4.315	4.28	4.33	4.305
22	17.99	18.00	4.85	4.82	4.835	4.69	4.69	4.690	4.75	4.79	4.770
23	17.99	17.98	5.45	5.43	5.440	5.28	5.27	5.275	5.27	5.28	5.275
24	18.00	18.00	4.87	4.88	4.875	4.73	4.72	4.725	4.70	4.63	4.665
25	17.99	18.11	3.12	3.13	3.125	3.00	2.95	2.975	3.05	3.03	3.040
26	18.01	18.01	3.24	3.28	3.260	3.11	3.11	3.110	3.15	3.15	3.150
27	18.01	18.00	3.48	3.43	3.455	3.32	3.30	3.310	3.34	3.33	3.335
28	17.98	18.04	3.38	3.39	3.385	3.22	3.27	3.245	3.25	3.25	3.250
29	18.04	18.05	3.95	3.93	3.940	3.80	3.80	3.800	3.83	3.82	3.825
30	18.07	18.06	3.64	3.67	3.655	3.50	3.51	3.505	3.56	3.53	3.545
31	18.01	18.02	3.23	3.21	3.220	3.12	3.06	3.090	3.15	3.16	3.155
32	18.05	18.02	3.41	3.41	3.410	3.24	3.24	3.240	3.26	3.28	3.270
33	17.98	18.00	6.43	6.43	6.430	6.30	6.30	6.300	6.41	6.40	6.405
34	18.05	18.02	6.11	6.13	6.120	6.00	6.00	6.000	6.05	6.05	6.050
35	17.99	18.00	3.20	3.15	3.175	3.10	3.00	3.050	3.08	3.09	3.085
36	18.02	18.03	3.87	3.89	3.880	3.72	3.72	3.720	3.78	3.78	3.780
Avge..	18.014	18.016			4.204			4.063			4.088

TABLE 2.

Percentages of fat found in milk by the Babcock, Roese-Gottlieb (Mojonnier), Adams and asbestos methods.

SAMPLE NO.	GRAMS TAKEN		BABCOCK—READING TO TOP OF MENISCUS			READING WITH GLYMOL			ROESE-GOTTLIEB (MOJONNIER)			ADAMS			ASBESTOS		
	A	B	A	B	Average	A	B	Average	A	B	Average	A	B	Average	A	B	Average
29	18.04	18.05	3.95	3.93	3.94	3.80	3.80	3.80	3.83	3.82	3.825	3.82	3.80	3.810	3.72	3.72	3.720
31	18.01	18.02	3.23	3.21	3.22	3.12	3.06	3.09	3.15	3.16	3.155	3.11	3.09	3.100	3.09	3.09	3.090
33	17.98	18.00	6.43	6.43	6.43	6.30	6.30	6.30	6.41	6.40	6.405	6.45	6.43	6.440	6.30	6.34	6.320
35	17.99	18.00	3.20	3.15	3.175	3.10	3.00	3.05	3.08	3.09	3.085	3.12	3.04	3.080	2.94	2.99	2.965
36	18.02	18.03	3.87	3.89	3.88	3.72	3.72	3.72	3.78	3.78	3.780	3.74	3.78	3.760	3.68	3.69	3.685
Average	18.008	18.02			4.129			3.992			4.050			4.038			3.956

TABLE 3.

Variations in percentages of fat found in milk by the Babcock method from those found by the Roese-Gottlieb (Mojonnier) method.

SAMPLE NO	READING TO TOP OF MENISCUS	READING WITH GLYMOL
1	+0.075	−0.075
2	+0.165	+0.005
3	+0.160	+0.045
4	+0.155	−0.010
5	+0.145	0.000
6	+0.135	−0.015
12	+0.090	−0.055
15	+0.150	+0.045
16	+0.125	−0.010
17	+0.085	−0.010
19	+0.160	+0.035
20	+0.075	−0.085
21	+0.110	+0.010
22	+0.065	−0.080
23	+0.165	0.000
24	+0.210	+0.060
25	+0.085	−0.065
26	+0.110	−0.040
27	+0.120	−0.025
28	+0.135	−0.005
29	+0.115	−0.025
30	+0.110	−0.040
31	+0.065	−0.065
32	+0.140	−0.030
33	+0.025	−0.105
34	+0.070	−0.050
35	+0.090	−0.035
36	+0.100	−0.060
Average..........	+0.116	−0.025

TABLE 4.

Variations in percentages of fat found in milk by the Babcock method from those found by the Roese-Gottlieb (Mojonnier), Adams and asbestos methods.

	READING TO TOP OF MENISCUS			READING WITH GLYMOL		
SAMPLE NO.	Roese-Gottlieb (Mojonnier)	Adams	Asbestos	Roese-Gottlieb (Mojonnier)	Adams	Asbestos
29	+0.115	+0.130	+0.220	−0.025	−0.010	+0.080
31	+0.065	+0.120	+0.130	−0.065	−0.010	0.000
33	+0.025	−0.010	+0.110	−0.105	−0.140	−0.020
35	+0.090	+0.095	+0.210	−0.035	−0.030	+0.085
36	+0.100	+0.120	+0.195	−0.060	−0.040	+0.035
Average....	+0.079	+0.091	+0.173	−0.058	−0.046	+0.036

CONCLUSIONS.

(1) The results obtained by the Babcock method reading to the top of the meniscus are higher than those obtained by any of the other methods used in this investigation.

(2) The results obtained by the Babcock method reading to the line of separation between the fat column and the overlying glymol agree more closely with those obtained by the other methods than do the results obtained by reading to the top of the upper meniscus.

(3) It would be advantageous to read the fat column to the line of separation between it and an overlying layer of glymol, (1) because of the distinctness of the line and the ease of reading and (2) because it conforms with the well-established practice of reading cream samples.

(4) The present specifications for conducting the Babcock test should be modified if the results here reported are confirmed by other workers and the writer suggests that similar work be done in laboratories in other parts of the country.

The following publications are also cited for reference:

Fifth Annual Report, Vermont State Agricultural Experiment Station, 1891

Vieth, P., Fat-free paper for use in Milk Analysis. Analyst, 1891, **16:** 127.

Liebermann, Leo and Székely, S, Neue Methode zur Bestimmung des Fettgehaltes der Milch. Z. anal. Chem., 1893, **32:** 168.

Röhrig, Armin., Verbesserter Apparat zur Milchfett-Bestimmung nach Gottlieb-Roese. Z. Nahr. Genussm., 1905, **9:** 531.

Nilson, L. F., Der Lactokrit im Vergleiche mit einigen anderen Methoden zur Bestimmung des Milchfettes. Chem.-Zeitung., 1891, **15:** 649.

Farrington, E. H. and Woll, F. W., Testing Milk and its Products.

Van Slyke, L. L., Modern Methods of Testing Milk and Milk Products.

Leach, Albert E , Food Inspection and Analysis.

REPORT ON SACCHARINE PRODUCTS.

By H. S. Paine (Bureau of Chemistry, Washington, D. C.), *Referee.*

Owing to delay in securing the necessary collaboration and to the fact that reports have not been received from all the collaborators, the Associate Referee on Honey is unable to present a final report at this meeting. It is recommended that the work outlined on honey be continued in expanded form next year.

No report has been received from the Associate Referee on Maple Products. It is recommended that steps be taken to have the work outlined on this subject actively prosecuted next year and brought to a definite conclusion.

A method which has important possibilities has recently been developed by F. W. Reynolds of the Carbohydrate Laboratory, Bureau of Chemistry, for simultaneous purification and concentration of enzymes. This method involves the use of a collodion ultra-filter of such permeability as to retain enzymes and at the same time permit the passage through the filter of water and various dissolved substances, including sugars, salts, pigments, etc. By this means, enzyme solutions can be washed with water on the ultra-filter until free from color, and can then be finally concentrated by permitting as much of the water acting as solvent to pass through the filter as is required in order to secure the desired degree of concentration.

This method has been very successfully applied to the concentration and purification of the enzymes invertase and melibiase. The latter is notoriously a weak enzyme, in the sense that it has heretofore been impossible to obtain concentrated and stable solutions of it. Nevertheless, this enzyme has now been obtained in highly active and stable form, and has been successfully employed in conjunction with invertase in the analytical determination of raffinose in beet molasses, invertase being first employed to produce cleavage of fructose from raffinose, and the enzyme melibiase being then used to hydrolize the resulting melibiose. Quantitative enzymic hydrolysis of raffinose and sucrose in beet molasses has been effected in as short a period as one-half hour, thereby permitting rapid and accurate analytical determination of raffinose by use of enzymes. Since beet molasses contains the two sugars, sucrose and raffinose, determination of these two sugars can be made simultaneously on the basis of the difference in change of polarization between two portions of a given sample, to one of which the enzymes invertase and melibiase have been added and to the second of which only the enzyme invertase has been added.

The enzyme method for the determination of raffinose and sucrose has been discussed in the foregoing detail since it is believed that the use of a concentrated and purified solution of the enzyme maltase has

important possibilities in solving the problem of the accurate determination of maltose in glucose and maltose sirups, permitting thereby the accurate determination of the other carbohydrate constituents.

O. S. Keener, appointed at the last meeting as Associate Referee on Maltose Products, resigned last May and H. C. Gore was appointed to succeed him. Owing to this fact, the work on maltose products has not been advanced as rapidly as would otherwise have been the case.

Adoption of the recommendations by the Associate Referee on Sugar-House Products is recommended.

No report on honey was made by the associate referee.

No report on maple products was made by the associate referee.

REPORT ON MALTOSE PRODUCTS.

By H. C. Gore (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*

None of the analytical methods so far proposed for the determination of maltose, dextrose and dextrines in products such as maltose sirup and glucose are sufficiently promising from the standpoint of accuracy and ease of manipulation to justify extended work in testing them.

The ideal method would be one which permits selective hydrolysis of maltose, without at the same time causing hydrolysis of dextrines. Enzymes are ideal reagents for the analysis of polysaccharides. Precise determination of maltose in mixture with dextrose and dextrines would apparently be possible if a sufficiently concentrated and stable preparation of the enzyme maltase were available. More extended use of enzymes such as maltase for analytical purposes would readily be possible if enzyme reagents of suitable character were available. This appears the more promising in view of the recent work of Willstätter[1] in improving existing methods for the extraction of maltase from yeast.

Your associate referee has commenced work along the lines indicated, but since he started his investigation about the first of June, subsequent to the resignation of O. S. Keener, formerly associate referee, and was able to devote only a portion of his time to this matter, he has not yet had opportunity to test thoroughly the possibilities of this method. It is recommended that investigation along the lines indicated be actively continued next year. While this proposal involves the working out of a new method, rather than the testing of a method already proposed, it is possible that the matter will lend itself to collaborative effort in certain of its phases at least.

[1] *Z. physiol. Chem.*, 1921, 111: 157.

THE DETERMINATION OF ASH IN CANE SIRUP AND MOLASSES.

By J. F. Brewster (Louisiana Sugar Experiment Station, New Orleans, La.), *Associate Referee on Sugar-House Products.*

The report of the previous Associate Referee on Sugar-House Products, F. W. Zerban[1], contained results of cooperative work on determinations of ash in cane sirup, first molasses and final molasses. These results were obtained by employing the three official methods[2] with slight modifications to ascertain (1) which of the three yields the most concordant results in the hands of different analysts, and (2) how well the results obtained agree.

The tabulated results showed that agreement among different analysts was not nearly so good as that between duplicates of the same analyst. This appeared to hold for all three methods.

In discussing the results, Zerban pointed out that no advantage is gained by the use of Method II (leaching the carbonized material) over Method I, the direct ash method, except when necessity compels. In regard to Method III (sulfated ash method), it was found that the amount of ash increased with the quantity of sulfuric acid used and also that the correction factor would vary with the purity of the product analyzed and is evidently nearer 20 per cent than the 10 per cent recommended in the official method. Zerban's report showed that the sulfated ash method has no advantage over the direct ash method from the standpoint of close agreement among different analysts or from that of ease of manipulation, and furthermore, that the sulfated ash method may give results widely divergent from those obtained by the direct ash method.

The present associate referee desires to report a continuation of the ash determination work based upon Zerban's conclusions and recommendations[3].

Three samples of sugar-house products—one a cane sirup, one a first molasses and one a final molasses—were sent to each collaborating analyst who was requested to determine the ash in each sample by the three methods published in Zerban's report and to incinerate at temperatures of 475°, 500°, 525° and 550°C., reporting the results for each temperature.

The four analysts who reported results and to whom the writer desires to express his thanks are the following: (1) S. H. Champlin, Cape Cod Preserving Co., Boston, Mass.; (2) H. Z. E. Perkins, American Sugar

[1] *J. Assoc. Official Agr. Chemists*, 1921, 4: 444.
[2] *Ibid.*, 1916, 2: 128.
[3] *Ibid.*, 1921, 4: 451.

TABLE 1.

Collaborative results on the determination of ash.

ANALYST	TEMPERATURE	METHOD 1*	METHOD 1†	METHOD 2*	METHOD 2†	METHOD 3 Platinum Dishes	METHOD 3 Silica Dishes
Cane sirup							
	°C.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1							2.43
							2.42
2						2.46	2.44
						2.51	2.45
3	475	2.26	2.25	2.27	2.30		
	500	2.23	2.28	2.13	2.15	2.56	
	525	2.26	2.19	2.08	2.09	2.53	
	550	2.20	2.17	2.04	2.06	2.52	
4	475	1.98	1.98				2.55
		2.05	2.10				2.49
		2.01	2.03				
		2.00	2.00				
	550	1.96	1.76				
		1.99	1.84				
		2.03	1.93				
		2.04	1.91				
First molasses							
1							5.59
							5.53
2						5.48	5.42
						5.59	5.48
3	475	4.90	4.93	4.95	4.91	...	
	500	4.90	4.89	4.46	4.45	5.72	
	525	4.76	4.85	4.77	...	5.66	
	550	4.68	4.71	4.66	4.68	5.67	
4							5.52
							5.45
Final molasses.							
1							9.02
							8.92
2						9.35	9.07
						9.16	9.10
3	475	7.96	7.88	7.69	7.49	...	
	500	7.73	7.74	7.73	7.77	9.37	
	525	7.77	7.88	7.65	7.57	9.16	
	550	7.69	7.39	7.61	7.53	9.23	
4	475	7.24	7.22				9.27
		7.25	7.25				9.28

*Without ammonium carbonate.
†With ammonium carbonate.

Refining Co., New Orleans, La.; (3) W. G. Raines, Jr., Louisiana Sugar Experiment Station, New Orleans, La.; (4) G. F. Snyder, Bureau of Standards, Washington, D. C.

The results are given in Table 1.

DISCUSSION.

It is seen at once that very good agreement occurs in the results of Method III reported by all the analysts, regardless of whether platinum or silica dishes had been used. The average sulfate ash in the sirup was 2.49 per cent; the lowest was 2.42 and the highest, 2.56. In the sample of first molasses the average is 5.55 per cent, with lowest and highest 5.41 and 5.67 per cent, respectively. In the sample of final molasses the average is 9.17 per cent, with lowest 8.92 per cent and highest 9.37 per cent. It happens that the lowest results were obtained with silica dishes and the highest when platinum dishes were used. The results of Analyst 2, who determined the ash by the sulfate method in both platinum and silica dishes, show in all cases that the figures are slightly lower when silica dishes were used. The differences in most cases may be only slight, but it seems advisable to recommend the use of platinum dishes.

Although very concordant results were obtained by the four analysts reporting at this time upon sulfated ash, such was not the case in the last report by Zerban[1]; in his report the disagreement among ten analysts was much greater, the maximum variation ranging from 0.35 per cent in cane sirup to 0.62 per cent in final molasses where the same amount of sulfuric acid had been used in ashing. It would not, therefore, appear justifiable to recommend exclusive employment of the sulfate method on the basis of satisfactory agreement among four analysts when such disparity had appeared among the results of ten.

Referring to the results for Methods I and II it is found that increasing the temperature at which the material is ashed shows a tendency to lower the results. This is readily noted by reading vertically down the columns of the table for Methods I and II, especially in the more concentrated products, while with cane sirup, using Method I, practically no differences are observed between temperatures of 475° and 550°C. For cane sirup, results for direct ash, using Method I, were reported only by Analysts 3 and 4. Each analyst was able to check his own results closely. However, there is a considerable disagreement between the results of the two analysts, the average for one being 2.19 per cent, for the other 1.97 per cent. These discrepancies are not likely to be due to differences in temperature.

The effects of higher ashing temperatures than those usually recommended are to be observed by reference to Table 1, Methods I and II,

[1] *J. Assoc. Official Agr. Chemists*, 1921, 4: 447.

where results for the more concentrated substances are shown. Even here the decrease in ash does not vary uniformly with increase of temperature. The results reported by Analyst 3 were obtained by use of a gas-heated muffle furnace; those of Analyst 4, with an electric furnace. It is well known that by use of an electric furnace of the type employed for ash determinations an oxidizing atmosphere is readily obtained, whereas with a gas-heated muffle—usually made of porous material and surrounded by combustion gases—the supply of air may be insufficient for complete oxidaton of the carbon formed although no unburned carbon may be detected by casual inspection of the ash. The discrepancies in the results cited may, therefore, be due to the use of two different heating devices and the consequent differences in air supply. The latter should be sufficient, particularly toward the end of the ashing, to insure complete removal of carbon. To this end a carefully controlled electric furnace is to be recommended.

Since ashing at the lower temperatures requires practically no more time than at the higher temperatures, the lower temperatures, 475° to 500°C., are to be recommended. What may be called incipient red begins at 475°C.; at 500°C. a distant dull red is attained. With an adequate air supply, ashing takes place rapidly at these temperatures.

If the results in Table 1 for direct and carbonated ash by Methods I and II are compared it would appear that no advantage is to be gained in an attempt to convert alkali earths to carbonates. The differences are negligible and seem just as likely to be lower after treatment with ammonium carbonate. In fact, in only 15 out of 33 cases is the carbonated ash higher, and then the differences are only slight.

In connection with the direct determination of ash in sugar-house products the paper by W. L. O. Whaley, read at this meeting, (page 370) demonstrates certain advantages in using nickel instead of platinum or silica dishes for the incineration.

Not only are the results concordant, but the ashing takes place more quickly than in platinum or silica dishes, and nickel has the obvious advantage of lower cost.

Returning to the subject of sulfated ash (Method III) it appears that the temperature of ashing makes practically no difference in the results unless, perhaps, when silica dishes are used. The presence of sulfuric acid may be counted upon to assist in the oxidation of carbon. However, the question of the proper conversion factor of sulfated ash to true ash must remain unanswered, so far as the present results are concerned.

The average results obtained by Methods I and II and those by Method III are shown in Table 2, with the factor for ascertaining the amount to be deducted from sulfated ash to convert the latter to true ash.

The variation in the conversion factor for the different products is seen at once by reference to Column 4 of Table 2 and, also confirming

TABLE 2.
Average results of determination of ash.

PRODUCT	METHODS I—II	METHOD III	FACTOR FOR CONVERTING SULFATE ASH TO TRUE ASH	FACTORS REPORTED BY ZERBAN
	per cent	*per cent*	*per cent*	*per cent*
Sirup	2.09	2.49	16.06	16.6
First molasses	4.77	5.55	14.05	17.6
Final molasses	7.47	9.17	18.54	18.9

the results reported by Zerban and others, it is seen to be much higher than the 10 per cent recommended in the official method. For sulfated ash where 0.5 cc. sulfuric acid had been used, the factors 16.06 for sirup and 18.54 for final molasses agree fairly well with those reported by Zerban, which were 16.6 and 18.9, respectively, while for the first molasses the factor given is 14.05 and that of Zerban is 17.6.

Although the results for sulfated ash given in this report show satisfactory agreement, it can not be argued, in view of the discrepancies reported by Zerban, that the sulfated ash method has any advantages over the direct ash method, particularly when the former is known to give results which may be widely at variance with the true ash content of the material analyzed.

RECOMMENDATIONS.

It is recommended—

(1) That Method I be given official preference for the determination of ash in cane sirups and molasses; and that Method II be used only when it is found impossible to get a carbon free ash by the shorter method.

(2) That Method III, the sulfated ash method, be discontinued as an official method.

Suggested Cooperative Work upon Sugar-House Products.

Our present methods for the determination of total solids in sugar-house products may be grouped under three heads, namely, drying methods, aerometric methods and methods employing the pycnometer. No doubt all these methods should be compared particularly with a view to establishing their reliability when applied to the analysis of the more concentrated products such as sirups, massecuites and molasses. To that end it is recommended that cooperative work be undertaken to compare the following methods:

1. Drying upon pumice stone.
2. Drying upon sand.
3. By means of the Spencer oven.
4. By means of a pycnometer—Walker, Newkirk (with Newkirk's method) or other type.

THE USE OF NICKEL DISHES FOR ASHING SACCHARINE PRODUCTS.

By W. L. O. WHALEY (Penick and Ford Laboratories, New Orleans, La.).

This investigation of the possibility of using nickel instead of platinum dishes for the ashing of saccharine products was undertaken primarily for the purpose of eliminating, if possible, the inconvenience and financial loss caused by occasional thefts of platinum which sometimes occur in spite of the constant vigilance which our own, in common with other laboratories, have to exercise to guard against such thefts. The results obtained are so satisfactory and of such general interest that it seems desirable to make them public.

A brief review of the subject of the estimation of ash in saccharine products reduces the choice really to two methods[1]: direct incineration and ignition with sulfuric acid.

In the direct incineration method the material, either with or without the addition of olive oil or water at some stage of the process, is directly ignited. In the other method the material after being subjected to preliminary charring with concentrated sulfuric acid is ignited and the residue weighed, after which an arbitrary correction to compensate for the conversion of chlorides, carbonates and other salts to sulfate is applied. Almost any text containing chemical methods for the analysis of saccharine products gives these two methods for the determination of ash, and generally 10 per cent is recommended as the correction to be applied to the sulfated ash. It has been shown conclusively by Zerban[2] and others that in most cases this 10 per cent deduction factor leads to incorrect results. If the varied composition of the different saccharine products on which an ash determination is made is taken into consideration it is not to be expected that a method which involves the use of any arbitrary correction of this kind will prove to be satisfactory. The work in our laboratories includes the examination of a great variety of saccharine products, differing in composition as much, for example, as a mixture of corn sirup with standard granulated sugar, with less than 0.25 per cent of ash, and the heaviest final or "black strap" molasses, with more than 10 per cent of ash. Any method of ashing used for products of every gradation in composition between these extreme types must be one that will give reasonably accurate results with any of these products. The sulfated ash method, in the opinion of the writer, does not meet this requirement and for that reason was not given further consideration.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 105; Browne, Handbook of Sugar Analysis, 1917, 495.
[2] *J. Assoc. Official Agr. Chemists*, 1921, 4: 444.

AVAILABLE DISH MATERIAL.

None of the various alloys used as platinum substitutes has proved very durable under constant use. The first sign of deterioration is usually the appearance of a speck; next an incrustation around this spot is seen and finally a pit is formed, in appearance something like a spring in a limestone country with a deposit of calcite built up around it. Alloy dishes require as much care as is given to platinum, and, unlike platinum, the damaged alloys have no market value. Consequently alloy dishes are very expensive when their durability is taken into consideration.

Silica dishes may be used for sulfated ash work but in ash determinations by the direct ignition method the silica is attacked by the alkaline constituents of the ash with liberation of carbon dioxide and consequent loss in weight of ash and progressive loss in weight of the dish.

Since nickel as well as silver dishes are used successfully in alkali fusions the recommendation to investigate the utility of nickel was accepted, and one dozen nickel dishes were obtained for this purpose.

EXPERIMENTAL

The new dishes were flat-bottomed, 5 cm. in diameter and 1.9 cm. in height, polished, and had a pure white metallic luster. They were given identifying marks and subjected to a preliminary heating. Iridescent colors appeared at once, but after heating for about 2 hours, cooling and desiccating, the dishes had the usual dull yellowish-gray appearance of used nickel ware. This coloring, followed by the change in appearance, did not look promising, but after the dishes were weighed, and the weights recorded, samples were weighed into them and ashed. Since the first ash results appeared concordant for the products used the use of the nickel dishes was continued, although at no time was the weight of any dish compared with its original weight until the laboratory sample numbers showed that 535 ash determinations had been made. In all these determinations a Hoskins Replaceable Unit Muffle Furnace was used for the final incineration. This furnace had been standardized previously by marking the positions of the rheostat lever when the furnace had attained and was maintaining a temperature of 427°C. (800°F.), 482°C. (900°F.), and 649°C. (1200°F.,) as indicated by a thermocouple pyrometer. Instead of the few drops of the less viscous olive oil usually recommended, a small piece of paraffin the size of a match head was added to the material being ashed. The paraffin does not spatter with products having an excessive moisture content, as does the oil, and is equally efficient for reducing frothing. After the paraffin was added, the samples were heated gently by applying a flame from above until the product was charred. This usually required less

than a minute. The dishes were then placed in the muffle furnace with the door left open to permit free access of air.

The ashes were burned at temperatures varying from 427°C. to 482°C., except occasionally with low grade products the temperature was raised to 538°C. (1000°F.). On two occasions the muffle door was inadvertently left closed and the temperature rose to nearly 1093°C. (2000°F.), fusing the ash. On these occasions the dishes were washed with a warm, dilute solution of sulfuric acid (1 volume of acid, sp. gr. 1.84, and 9 volumes of water), and again heated to 649°C. before being used again.

After 535 ash determinations had been made in these 12 nickel dishes the dishes were cleaned with the dilute sulfuric acid previously mentioned, heated at 649°C., desiccated and weighed. The appearance of the dishes remained the same as after the first heating to which they were subjected before being used. Since all the dishes had been used to approximately the same extent, it is safe to assume that at least 40 ash determinations had been made in each. Data showing the loss in weight of the dishes and the calculated effect of this upon the ash determinations are given in tabular form below. Column 1 of the table shows the identifying marks on the dishes; Column 2, the initial weights of the dishes after the preliminary heating; Column 3, the weights after at least 40 ash determinations had been made in each; Column 4, the difference in milligrams between these weights; and Column 5, this difference expressed in percentage of the original weight. In Column 6

Data showing change in weight of nickel dishes when used for the ashing of sirups and molasses by the direct ignition method and the effect of this change in weight upon the ash results.

DISH	INITIAL WEIGHT	FINAL WEIGHT	DIFFERENCE		AVERAGE CHANGE IN WEIGHT PER DETERMINATION	PERCENTAGE OF SAMPLE	
						6-Gram Charge	1-Gram Charge
	grams	*grams*	*milligrams*	*per cent*	*milligrams*		
No. 1......	26.4470	26.4555	+8.5	0.032	+0.21	0.0035	0.021
No. 2......	28.3011	28.3080	+6.9	0.024	+0.17	0.0029	0.017
No. 3......	27.1889	27.1752	−13.7	0.050	−0.34	0.0057	0.034
No. 4......	27.9964	27.9960	−0.4	0.001	−0.01	0.0002	0.001
No. 5......	26.0603	26.0552	−5.1	0.020	−0.13	0.0022	0.013
No. 6......	26.5366	26.5220	−14.6	0.055	−0.37	0.0062	0.037
o..........	28.4808	28.4800	−0.8	0.003	−0.02	0.0003	0.002
oo.........	26.0806	26.0715	−9.1	0.035	−0.23	0.0038	0.023
ooo........	27.7479	27.7306	−17.3	0.062	−0.43	0.0072	0.043
ooo o|........	26.3412	26.3394	−1.8	0.007	−0.05	0.0008	0.005
ooo oo........	26.8934	26.8854	−8.0	0.030	−0.20	0.0033	0.020
ooo ooo........	26.9952	26.9900	−5.2	0.019	−0.13	0.0022	0.013
Total....	325.0694	325.0088	−60.6	0.019	......	....	......
Average..	27.0891	27.0841	−5.1	0.019	−0.13	0.0022	0.013

is given, in milligrams, the average change in weight per determination, on the assumption that the dish had been used for 40 determinations. The dishes were of such size that with corn sirup which intumesces violently one gram is the maximum weight that can be burned safely while with a final molasses six grams may be used. Columns 7 and 8 of the table give the percentages of a 6-gram charge and a 1-gram charge, respectively, which this average change in the weight of the dish represents.

DISCUSSION.

It was observed at once when the use of these nickel dishes was begun that the time required to burn the charge completely to a gray ash was very short. Only 15 to 20 minutes was required for a high-grade molasses or sirup. On four different occasions the same charge of the same product was ashed in platinum dishes in the same muffle and at the same time. The difference in the ash results was in no case as great as 0.1 per cent and the time required for complete incineration in platinum was sometimes twice as long as that necessary for complete incineration in the nickel dishes.

It was thought that the rapidity with which the sample burned in the nickel dishes might be caused by the catalytic action of oxides of nickel formed but the appearance of the dishes at the conclusion of the tests and the slight losses in weight shown do not seem to justify this assumption since no material oxidation of the nickel could have occurred.

The results here reported appear to show that nickel dishes can be used with entire satisfaction for the direct ignition of saccharine products in control work. The accuracy of the results is comparable with that obtainable when platinum dishes are used, and the initial cost is only about 2 per cent of that of platinum. Nickel dishes are far superior to dishes made of fused silica for work of this kind and cost only about two-thirds as much.

Committee on nominations: R. W. Balcom of Washington, D. C., J. B. Weems of Virginia, and J. W. Kellogg of Pennsylvania.

Committee on resolutions: B. B. Ross of Alabama, H. B. McDonnell of Maryland, and G. L. Bidwell of Washington, D. C.

Auditing committee: C. M. Bradbury of Virginia and J. B. Reed of Washington, D. C.

Committee to wait upon Secretary of Agriculture: J. B. Weems of Virginia, W. W. Skinner of Washington, D. C., and H. C. Lythgoe of Massachusetts.

Committee to wait upon Honorary President: J. K. Haywood of Washington, D. C. and R. N. Brackett of South Carolina.

Committee to wait upon Senator Ladd: W. W. Skinner of Washington, D. C., G. S. Fraps of Texas, and C. H. Bailey of Minnesota.

FIRST DAY.

WEDNESDAY—AFTERNOON SESSION.

REPORT ON FERTILIZERS.

By R. N. Brackett (Clemson Agricultural College, Clemson College, S. C.), *Referee.*

J. M. Bartlett, Orono, Maine, was designated as Associate Referee on Boric Acid in Fertilizers and Fertilizer Materials by the Committee on Recommendations of Referees. As W. H. Ross had been actively and efficiently working on one phase of this problem, your referee took the liberty, by the authority he supposed was vested in the general referee, to add him as an associate referee to cooperate with Bartlett, which arrangement was accepted.

With regard to the recommendation of the Associate Referee on the Preparation of Ammonium Citrate Solution the committee strongly commended the work done but stated that objections to the final adoption of the proposed method as the exclusive official method had been presented to the committee by several members of the association, it being contended, among other objections, that the working details of the method are not sufficiently definite and explicit in certain particulars, and that it is essential that more definite detailed directions be given before final adoption of the method as official.

It may also be said that inasmuch as C. S. Robinson had done much excellent work on the problem of the availability of nitrogen, your referee took the liberty to request that he act as Associate Referee on the Availability of Organic Nitrogen and make such recommendations as seemed to him desirable to modify the present methods of the association and suggest a statement as to limits of accuracy. This work will be necessary for incorporation in the revised edition of the Methods of Analysis.

As it seemed to be the general opinion of the members of the association at the last meeting that a considerable amount of work had already been done by and presented to the association, the Associate Referee on Potash has prepared a paper which will be presented as a part of his report, setting forth the present status of the question raised by H. C. Moore, as to the strength of alcohol to be used in washing the precipitate in the Lindo-Gladding method. This preliminary review appeared to be highly desirable, if not absolutely necessary, before actually taking up the problem and sending out samples for collaborative work, especially when most laboratories have been working short-handed

and can ill afford to undertake any additional burdens unless they are shown to be really worth while.

After carefully studying the method offered by Elmer Sherrill, the associate referee concluded that this method, while no doubt useful as a factory control method, was not suitable as an official method. Therefore no collaborative work was advised. Your referee concurs.

You are no doubt aware that F. B. Carpenter presented a paper[1] before the Fertilizer Division of the American Chemical Society at the Pittsburgh meeting in September, again raising the question as to the failure of the Lindo-Gladding method to show all the potash in certain mixed fertilizers, and suggesting that this association again take up this question and endeavor to make such modifications of the Lindo-Gladding method as may be necessary to perfect it in this respect. The associate referee has considered this paper in his report.

In a letter received from A. G. McCall, under date of April 8, the Associate Referee on Potash Availability recommends that he be relieved from duty, inasmuch as the potash situation does not seem to warrant any further work on this subject.

Your referee received, through R. W. Balcom, a letter from the United Chemical and Organic Products Co., asking whether public chemists could properly use a 1-gram charge in determining the insoluble in "precipitated pure bone". A negative reply was given as the recommendation had been read only once, and the method was not, therefore, official.

The following matters have also been brought to the attention of the referee:

Insoluble phosphoric acid.—The importance of strictly following the directions given in the official method for washing the fertilizer before treating with ammonium citrate solution by H. C. Moore, Armour Fertilizer Works, Chicago. Some interesting results obtained by W. R. Austin of Armour's Nashville plant were submitted. The subject does not seem to call for any work by the association.

Iron and alumina determination in phosphate rock.—This subject was brought up before the last annual meeting of the association by some of the fertilizer chemists, and the question was raised as to the desirability of incorporating a method in the forthcoming revised edition of the Methods of Analysis. In April, a letter from the J. H. Pratt Laboratory, Tampa, Fla., was referred to your referee by R. W. Balcom. It called attention to the fact that no method was given in the Methods of Analysis, and asked whether any steps had been taken by the association toward the adoption of such a method. The question of collaborative work on this problem was also raised at the last annual meeting of this

[1] *Am. Fertilizer*, 1922, 57: 55.

association. Some of the members, including your referee, thought that sufficient work had already been done on this problem to warrant action at this meeting. Therefore, a brief paper has been prepared in which an attempt has been made to gather together all the work done by and presented to the association on this subject. If the presiding officer consents, this paper will be presented. The members of the association can then discuss the matter and come to a decision as to what should be done about adopting a method or taking up work.

Potash in mixed fertilizers.—This has already been referred to in connection with the associate referee's work on potash. This matter, as you know, has been brought up before the association several times in the past, especially by the fertilizer chemists, and perhaps it would be well to discuss the question briefly and decide whether or not any action is necessary.

"*Basic Phosphate*".—A question of definition and designation was raised by E. W. Magruder of the F. S. Royster Guano Co., Norfolk, Va., in reference to mixtures of calcium carbonate and acid phosphate This question properly belongs within the jurisdiction of the Committee on Definitions of Terms and Interpretation of Results, to which it will be referred.

Authority of the general referees in the appointment of associate referees.—W. W. Skinner, the secretary, has suggested that this question be brought before the association inasmuch as there seems to be some misunderstanding on the part of some of the general referees as to the limits of their authority in this regard. Permission is requested of the presiding officer to bring this question up at an appropriate time.

The discussion relating to the authority of the general referee to appoint associate referees was opened by R. N. Brackett Friday afternoon, and it will be found in the published proceedings of that day.

SUMMARY OF WORK ON THE DETERMINATION OF IRON AND ALUMINA IN PHOSPHATE ROCK BY THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

By R. N. Brackett (Clemson Agricultural College, Clemson College, S. C.)

The first reference to a method for determining iron and alumina in phosphates was found in the proceedings of the 8th Annual Convention, 1891, in a paper entitled, "Proposed Method for the Analysis of Native Phosphates Containing Iron and Aluminum", by L. W. Wilkinson, Auburn, Ala., in which it was stated: "The discovery in Florida of native phosphates containing iron and aluminum demands that the association adopt a method for the analysis of these phosphates". Then follows a method which, it is also stated, gave satisfactory results.

The abstracts relating to analytical work in this volume of the proceedings also contain the abstract of a paper by R. Jones, "Estimation of Iron and Alumina in Phosphates"[1]. The method was a modification of the Glaser method.

No reference to this subject was made in the proceedings of the 9th Annual Convention, 1892.

In the proceedings of the 10th Annual Convention, 1893, in his report on phosphoric acid, R. J. J. De Roode says: "The second subject which was taken up for investigation was the determination of iron and alumina in phosphates. Now, although I was aware of the fact that this subject did not come under the duties of the reporter on phosphoric acid, I felt that, owing to the numerous requests for investigation on this subject, something ought to be done". Sample No. 2 (a powdered Florida phosphate rock) was prepared especially for this purpose, and the results of the determination of iron and alumina were given. The author says further: "These results admit of no conclusion as regards the best method, and there is nothing to show which method gives results which are nearest the truth. In my opinion, the method of Mr. Charles Glaser[2], of the firm of Lehman & Glaser, Baltimore, is a good one.

"It is the opinion of some of the members of this association that the determination of iron and alumina in phosphates is without the province of the investigations of this association. I, however, am of a different opinion, and since this is a subject upon which the greatest controversies have arisen among chemists, I deem it the duty of the Association of Official Agricultural Chemists to take up the matter for exhaustive investigation, and to establish, if possible, a reliable method for the estimation of iron and alumina in phosphates, to be considered as an official method in the same light in which our other methods are official, and I would recommend that a special reporter be appointed next year for this purpose". De Roode's recommendation (7th) was as follows: "That a special reporter be appointed for next year whose duty it shall be to institute investigations upon the subject of the determination of iron and alumina in phosphates".

The list of reporters for 1893–1894 does not contain any reference to a special reporter on this subject, because, after a discussion, De Roode's 7th recommendation was not adopted. De Roode stated: "There seems to be some disagreement among the members of this association as to whether that is within the province of the work we are doing. I would like to have that question decided. If it be declared that this matter is within the scope of our labors, some measures should be taken which will render it unnecessary for the reporter on phosphoric acid to do all this work".

---

[1] *Z. angew. Chem.*, 1891, **4**: 3.
[2] *Z. anal. Chem.*, 1892, **31**: 382; *Pharm. Review*, Baltimore, 1892, **1**: 185.

As a result of the discussion in which Chazel and McDonnell (H. B.) took part, it was decided that this was not a matter for the association.

The only reference to this subject contained in the proceedings of the 11th Annual Convention, 1894, was in abstracts of papers.

During the 12th Annual Convention, 1895, in a discussion of a report on methods of the A. O. A. C. for phosphoric acid, A. A. Persons, Lake City, Fla. raised the question: "Would it not be in order to say something in regard to the estimation of iron and alumina in phosphates?" He suggested a method. H. A. Huston admitted the desirability and importance of a method, stating that all methods so far gave varying results. W. D. Bigelow referred to recent experiments seen at A. A. A. S. meetings, in which thioacetic acid was used. R. J. Davidson referred to the method suggested by Wilkinson. No action was taken by the association.

At the 13th Annual Convention, 1896, the Committee on Recommendations of Reporters recommended "that the methods for iron and alumina in phosphates be referred to the reporter (on phosphoric acid) for 1897".

At the 14th Annual Convention, 1897, H. B. McDonnell, Reporter on Phosphoric Acid, gave results reported on the following methods for iron and alumina in phosphates: acetate, thiosulfate, and Glaser. Samples sent out were the following: South Carolina rock, Florida rock, Alabama rock, Pottstown slag, and a solution of chemically pure salts. Seven or eight collaborated. Comment of referee: "The results are too few by any of the methods to admit of much comparison or the drawing of very definite conclusions. There are more results reported on iron by the permanganate method than by any other, and with a few exceptions they agree fairly well. This seems to be the best method for the determination of iron in phosphates. The most promising method for alumina, in my opinion, will be found to be that of Gladding, potash method. I would recommend that the work be continued next year". A paper by C. W. Lehmann, "Estimation of Iron and Alumina in Mineral Phosphates (Iron by Sodium Peroxide, Aluminum as Phosphate)", appears in these proceedings. The Committee on Recommendations of Referees recommended: "In regard to iron and alumina, that methods for determination of these substances in phosphates be further investigated". Adopted on motion of M. A. Scovell.

There was no reference to this subject in the proceedings of the 15th (1898) and 16th (1899) Annual Conventions of the association.

In the proceedings of the 17th Annual Convention, F. G. Runyan reported that three samples were sent out for iron and alumina in phosphates. The methods tried were the modified acetate for combined iron and aluminum phosphates, phenylhydrazine for aluminum, and permanganate for iron in separate portions of solution.

After discussing the results of the collaborative work Runyan said: "The subject of the determination of iron and alumina in phosphates is one that, in my opinion, may well receive some attention from the members of this association during the coming year".

In the proceedings of the 18th Annual Convention, 1901, H. K. Miller, Florida, Referee on Phosphoric Acid, reported that three samples were sent out for iron and alumina in phosphates, as follows: basic slag, ground phosphate, and a solution of chemically pure salts; that the methods used were the acetate and molybdate; and that results were obtained from eight collaborators. The results were discussed as follows: "As usual few results were reported on iron and alumina, and as is generally the case, quite varying results have been obtained. It would evidently be unwise to make any recommendations based on the results which have been reported on these samples".

There was no reference to this subject found in the proceedings of the 19th (1902), the 20th (1903) and the 21st (1904) Annual Conventions.

At the 22nd Annual Convention, 1905, E. W. Magruder, Referee on Phosphoric Acid, had no report to present, but recommended that work be done on the determination of iron and alumina in phosphates, looking to the adoption of an official method. Committee A recommended that the subject of an accurate determination of iron oxide and alumina in rock phosphates be examined by the Referee on Phosphoric Acid and an official method be recommended to the association the following year. (Motion by T. S. Gladding referred to the committee.)

At the 23rd Annual Convention, 1906, J. M. McCandless, Associate Referee on Phosphoric Acid, who had agreed to undertake the investigation of iron and alumina in phosphates, reported that three prepared solutions were worked on in his own laboratory. The best results were obtained by the acetate method by Gladding and the Glaser method. This report brought out remarks by F. P. Veitch and others on previous work which had been done on this subject, but Committee A made no recommendation.

At the 24th Annual Convention, 1907, McCandless again made a report on this subject. The samples sent out were: No. 1, a synthetic mixture; No. 2, Tennessee rock. Methods used for alumina: thiosulfate method modified, Gladding method, Glaser method; for iron, any volumetric method preferred. Only two collaborators reported on Sample No. 1 and four reported on No. 2. During the discussion, W. F. Hand gave a method which had given good results in his laboratory.

Certain comments by the associate referee and a supplementary report by F. B. Carpenter on this subject followed. Committee A made no recommendation apparently, but at the 25th Annual Convention, 1908, McCandless, Referee on Phosphoric Acid, made another

report on this subject, which he said was in accordance with a recommendation of the association at its previous convention. He reported that three samples (Florida rock, Tennessee rock and a synthetic solution) had been sent out to ten chemists. The methods used were the Gladding, the Glaser, and a proposed modification of the acetate method. Six collaborators reported results.

In his remarks McCandless stated: "On the whole the results seem to be encouraging and to show that all three of the methods for which instructions were sent are capable of giving good results. The referee would call attention to the fact that this subject has been taken up by the National Fertilizer Association, and would recommend cooperation between the next referee and the committee of that association, with a view to reaching a decision as to what method shall be adopted".

There was no reference to this subject in the proceedings of the annual conventions from the 26th to the 37th, inclusive.

As a conclusion of the whole matter, it may be said that the collaborative work which has been undertaken by this association from time to time was done only in a half-hearted way, because the subject of determining iron and alumina in phosphates has never appealed to the members as being of any real importance to them. The members of this association were never called upon to make determinations of iron and alumina in phosphates in the course of their inspection work. The interest in this subject was limited to the buyer and seller of phosphate rocks and in no way concerned the members of this association in their regulatory work.

Therefore, in presenting this paper, your referee recommends, first, that the association decide at this meeting whether or not it wishes to undertake work on this subject; and second that, if so, a special referee be appointed on this subject.

It was moved that no further work be undertaken at this time in regard to the determination of iron and alumina in phosphate rock, as it was considered that this was not properly the work of the association.

The motion was seconded and carried.

REPORT ON BORON IN FERTILIZERS.

By J. M. Bartlett (Agricultural Experiment Station, Orono, Maine), *Associate Referee.*

The Referee on Borax in Fertilizers for 1921 recommended that some modification of the distillation (Bartlett) method[1] be worked out for determining water-soluble boron, as the method in its present form gives not only water-soluble boron but that which is dissolved by weak acids.

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 90.

It is well known that there are several compounds of boron which are only slightly soluble in water but very soluble in weak acids, and should any of these compounds occur in fertilizers or fertilizing materials it would be very important to know whether they are as injurious to plants as the more soluble compound.

It seemed best, therefore, to experiment with some of these compounds before suggesting any change in the method since the object desired is to determine the boron which is injurious to plants rather than water-soluble boron.

W. H. Ross of the Bureau of Soils very kindly furnished the writer for this purpose four minerals carrying boron, and some experiments were carried out in the station greenhouse with bean plants which are quite susceptible to boron injury.

The minerals used were Colemanite, a hydrated calcium borate, having the formula $Ca_2B_6O_{11}.5H_2O$; Ulexite, also a hydrated mineral represented by the formula $Na\,Ca\,B_5O_9 . 8H_2O$; Howlite, a borosilicate of calcium having a formula of $H_5Ca_2B_5SiO_{14}$ and a sample of Tourmalin, said to contain about 10 per cent of boron trioxide. All these minerals were pulverized fine enough to pass a 60-mesh sieve for analysis and use in the experiment. They are supposed to be insoluble in water but when treated with 50 cc. of hot water on the steam bath for 20 minutes about one-third of the boron in the Colemanite, nearly all that in the Ulexite and about one-third of that in the Howlite was dissolved. The Tourmalin, of course, was not acted on at all, either by hot water or weak acid. When one-half cc. of strong hydrochloric acid was added to the 50 cc. of hot water the first three minerals mentioned were readily dissolved. The following table shows the amount of boric acid found by the different methods of treatment.

Amount of boric acid found by the three different methods.

MINERALS USED	SOLUBLE IN WATER	SOLUBLE IN WEAK ACIDS	
	Ross-Deemer Method	Modified Ross-Deemer Method*	Bartlett Method
	per cent	*per cent*	*per cent*
Colemanite.....	28.48	86.66	86.66
Ulexite........	69.69	70.29	69.69
Howlite..	30.30	80.60	73.33
Tourmalin.....	0	0	0

*One-half cc. strong hydrochloric acid was added to the 50 cc. of hot water used to dissolve 0.1 gram of the mineral.

PLAN OF THE EXPERIMENT.

The soil used was from a pasture that had not been cultivated or fertilized for years. The fertilizer applied was a 5–8–7 goods which

was free from boron. Nine-inch pots were employed, three being allowed for each mineral, and three checks to which only fertilizer was applied. Borax was applied to three pots for comparison with the other minerals. The same amount of fertilizer was used in each pot, and the boron minerals were added in units sufficient to equal 10, 20 and 40 pounds of anhydrous borax to the ton of fertilizer. The fertilizer and minerals were weighed out separately, but were thoroughly mixed before being applied to the soil. The fertilizer was also thoroughly mixed with the earth below where the beans were planted. Four seeds were put in each pot and nearly all came up at about the same time. They grew and looked healthy for the first six days, when those containing the fertilizer carrying the equivalent of 40 pounds anhydrous borax to the ton began to show very serious borax injury; those carrying 20 pounds also showed some injury.

The injury at this time was most marked in the pots containing borax and Ulexite. The plants in the pots carrying 10 pounds of anhydrous borax to the ton of fertilizer were about as thrifty as those with none, but the leaves were a little lighter color. At the end of two weeks more the plants in the pots containing the largest amount of boron showed extensive injury with all the minerals except the Tourmalin. The leaves turned yellow and the lower ones died and dropped off. The plants in the pots with less boron, 20 pounds of anhydrous borax to the ton of fertilizer, began to show considerable injury, the leaves being lighter color and dying around the margins, particularly the lower ones. The only differences noticeable in the plants in pots where the smallest amount of boron was used (10 pounds of anhydrous borax to the ton of fertilizer) and those having none, were some yellow spots in the leaves and some leaves slightly affected around the margins. Throughout the remainder of the experiment no difference could be detected in amount of injury to the plants whether the boron was applied in the form of borax or the less soluble forms of Colemanite, Ulexite or Howlite. The plants with the largest amount of boron died after reaching the height of six to eight inches. Those with the next largest amount attained about two-thirds the size of the check plants and matured a few pods but showed a good deal of injury. The set grown on the smallest amount grew nearly as large as the checks but did not develop as many pods; many of the leaves showed yellow spots and slightly yellow margins. The pots containing the Tourmalin grew plants as healthy as the checks; at all times they were good color and showed no boron injury.

RECOMMENDATIONS.

It is recommended—

(1) That as boron compounds not soluble in water but soluble in weak acids appear to be as injurious to plants as the water-soluble com-

pounds and the distillation method, as now carried out, determines the boron in such compounds, it be adopted as an official method in its present form to determine boron in mixed fertilizers and fertilizer materials.

(2) That in using the Ross-Deemer[1] method for the determination of boron in fertilizer materials known to contain boron compounds not soluble in water but soluble in weak acids, sufficient hydrochloric acid be added to make the 50 cc. of water used in the first digestion on the steam bath to bring the boron into solution, distinctly acid throughout the digestion. This is recommended for further study.

(3) That the Ross-Deemer method, as given by the referee for 1921, be adopted as an official method to determine water-soluble boron in mixed fertilizers and fertilizer materials.

REPORT ON THE PREPARATION OF A NEUTRAL SOLUTION OF AMMONIUM CITRATE.

By C. S. Robinson (Agricultural Experiment Station, E. Lansing, Mich.), *Associate Referee.*

Three recommendations were made by the associate referee at the last meeting of the association dealing, respectively, with the definition of a neutral solution of ammonium citrate, the method for the preparation of such a solution and the methods for its analysis[2]. After studying the discussion of the report and consulting by letter with the Chairman of Sub-Committee A and with the Referee on Fertilizers it was decided to limit collaborative work to the last point, *i. e.*, the methods of analysis of citrate solutions. Changes have been made in the first two recommendations to conform to suggestions made regarding them.

Before proceeding to an inspection of the results secured in the collaborative work the associate referee desires to discuss briefly certain suggestions that have been made by various members of the association during the past two years. The question which perhaps comes up most frequently is that concerning the desirability of controlling the reaction of ammonium citrate solutions. In other words, do variations in the reaction of the citrate solutions affect the results obtained in actual analysis sufficiently to warrant an accurate adjustment of the reagent? This question has been asked probably at every meeting at which a report on the subject of neutral ammonium citrate solutions has been made. But it was definitely brought to the attention of the present associate referee this year with the suggestion that he secure samples

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 327.
[2] *Ibid.*, 445

of solutions actually being used in several laboratories and use them for analyzing samples of phosphates to settle this point. The suggestion was not followed out because the writer feels that he has already answered the question more satisfactorily than could be done in the manner suggested. A number of years ago he prepared four solutions of ammonium citrate having reactions pH 6.6, 7.0, 7.4 and 7.8, *i. e.*, varying from acid to alkaline and including the two "neutral" solutions. A dozen different materials of varying phosphate content were analyzed by the usual procedure using these solutions. The results have been reported[1]. While variations in the results were observed they were in most cases small and within the limits of experimental error. Nevertheless, the fact remains that some differences were noted; hence the possibility must be confronted of the existence of products sufficiently susceptible to alkali to be affected by differences in reaction.

A second objection which is frequently made to the accurate adjustment of the reaction of this reagent is that such work is fruitless since the reaction changes during the determination. The writer also has considered this point. So far as he is aware there exists only one piece of experimental evidence supporting the contention. In that work a current of air was passed through the flask during the digestion to remove the ammonia liberated. The result naturally followed that ammonia was lost. A review of the work done in past years will show that this point received attention in preparing the official method which accordingly prescribes that the flask be "loosely stoppered". In the work of the writer the reactions of the solutions were carefully determined before and after the analyses, which, as stated, were carried out exactly as prescribed by the official method except for the reaction of the solutions. It was very definitely shown that with strictly neutral or acid solutions *no change in reaction takes place.* Alkaline solutions tend to become neutral.

In view of these facts it appears advisable to control the reaction of the reagent with some care. Methods now available make it possible to do this with the ease and accuracy with which any standard reagent can be prepared.

As stated in last year's report, the determination of the composition of citrate solutions by analysis is influenced by the analytical procedure used. A study of the more common analytical methods in vogue in various laboratories was made, and the results, which have been published elsewhere[2], were made the basis for the collaborative work. This work consisted in the analysis by five different methods of three samples of citrate solutions prepared by the associate referee and sent out to collaborators.

---

[1] Michigan Agr. Expt. Sta. Tech. Bull. 46, 20.
[2] *J. Ind. Eng. Chem.*, 1922, 14: 429.

Solution A was prepared so as to have a ratio of ammonia to citric acid of 1:4.25 as determined by the formaldehyde method.

Solution B was made to have a pH of 7.0 using the colorimetric method with phenol red as the indicator, as recommended in last year's report.

Solution C was neutralized electrometrically and should correspond in composition to a solution of triammonium citrate.

The methods of analysis were described as follows:

Pipet 50 cc. samples of the solutions submitted into 500 cc. volumetric flasks and make up to the mark with carbon dioxide-free distilled water. Use these solutions for analysis.

Method I.

REAGENTS.

0.25N alkali, 0.5N acid, and 0.1N alkali.

Ammonia.—Transfer 25 cc. samples to distillation flasks, add 40 cc. of 0.25N alkali to each and distil 45–50 cc. into receiving flasks containing 20 cc. of 0.5N acid. Titrate back with 0.1N alkali, using cochineal as indicator.

Citric acid.—Wash the residue from the distillation flask into an Erlenmeyer flask and add a few drops of phenolphthalein solution and sufficient 0.5N acid to decolorize the solution. Titrate back with 0.1N alkali.

Method II.

REAGENTS.

0 1N alkali and 0.1N acid.

Ammonia.—Transfer 10 cc. samples to distillation flasks, add 40 cc. of 0.1N alkali and 20 cc. water to each and distil about 50 cc. into receiving flasks containing 50 cc. of 0.1N acid. Titrate back with 0.1N alkali, using methyl red or cochineal as indicator

Citric acid.—Wash the residue from the distillation flask into an Erlenmeyer or other flask suitable for use in titrating and add a few drops of phenolphthalein solution and sufficient 0.1N acid to decolorize it. Titrate back with 0.1N alkali.

Method III.

REAGENTS

0.1N alkali, 0.1N acid, and methyl red indicator.

Ammonia.—Transfer 10 cc. samples to distillation flasks, add 40 cc. of 0.1N alkali and 200 cc. of water and distil about 150 cc. into receiving flasks containing 50 cc. of 0.1N acid. Titrate back with 0.1N alkali, using methyl red or cochineal as indicator.

Citric acid.—Wash the residues from the distillation flask into Erlenmeyer or other flasks suitable for use in titrating, add a few drops of methyl red solution and sufficient 0.1N acid to produce a *permanent* red color. (Just enough methyl red solution should be used to enable the analyst to detect the pink color. Too much tends to obscure the final end-point with phenolphthalein.) Boil, add a few drops of phenolphthalein solution and titrate back with 0.1N alkali to an end-point with this indicator.

Method IV.

REAGENTS.

0.5N sodium hydroxide and 0.5N sulfuric acid.

Ammonia.—Transfer 50 cc. samples to distillation flasks, dilute with 200 cc. of distilled water (neutral to phenolphthalein) and add 35 cc. of 0.5N sodium hydroxide (40 cc. with Solution A). Distil and collect the ammonia in 35 cc. of 0.5N sulfuric acid.

Citric acid.—Wash the residue from the distillation flask into one suitable for use in titrating, add a few drops of phenolphthalein and titrate to the disappearance of color with 0.5 sulfuric acid.

Method V.

REAGENTS.

0.1N alkali, 0.1N acid, and formaldehyde solution, 40%, neutral to phenolphthalein.

Ammonia.—Use results from one of the preceding methods, stating which one.

Citric acid.—Pipet 25 cc. of each citrate solution into 250 cc. volumetric flasks and dilute to the mark. Transfer 10 cc. to a flask suitable for use in titrating, add 4 cc. of the formaldehyde solution and titrate the acid liberated, using 0.1N alkali and phenolphthalein.

Four determinations by each method on each solution were requested with the intention of using the three agreeing most closely for this report. In the following table are given the average values and the maximum experimental errors observed.

The following analysts cooperated in the work. The corresponding numbers are used in the table.

1. C. S. Robinson.
2. S. L. Bandemer, Michigan Agricultural Experiment Station, E. Lansing, Mich.
3. E. J. Miller, Michigan Agricultural Experiment Station, E. Lansing, Mich.
4. O. B. Winter, Michigan Agricultural Experiment Station, E. Lansing, Mich.
5. E. E. Vanatta, University of Missouri, Columbia, Mo.
6. Swift & Co., Union Stock Yards, Chicago, Ill.
7. R. D. Caldwell, Armour Fertilizer Works, Atlanta, Ga.
8. R. C. Charlton, 211 E. North Ave., Baltimore, Md.

DISCUSSION.

Ammonia.—The procedures used naturally divide themselves into two groups: (1) Those involving the distillation of about 50 cc. of liquid (Methods I and II); and (2) those in which approximately 150 cc. of distillate were collected (Methods III and IV). The latter group corresponds to the present official method[1]. Apparently Methods III and IV give more concordant results. They are somewhat higher than the

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 6.

first two, probably because of a more complete washing out of ammonia from the apparatus by the larger volume of distillate.

Citric acid.—The question which was provocative of the present discussion was, however, the method of procedure for the determination of the citric acid. In the work already referred to[1] it was shown that Methods III and V checked each other and gave accurate results, while the other methods gave values which were too high, although Method I approached closely to the correct ones. These conclusions are substantiated by the results of the collaborative work. On all three solutions the agreement between Methods III and V is good, while all other results are higher in value. The conclusion from previous work that the low results are the correct ones is verified by the figures for the ratio of ammonia to citric acid on Solution C. This solution was prepared

Collaborative results on the analysis of ammonium citrate solutions.

CITRIC ACID (grams per liter).

	Analyst	Method I		Method II		Method III		Method IV		Method V	
		grams	*diff.*	*grams*	*diff.*	*grams*	*diff.*	*grams*	*diff.*	*grams*	*diff.*
Solution A	1	226.80	0.80	235.90	0.90	230.90	0.20	231.90	0.10	229.00	0.00
	2	230.58	0.05	233.00	0.64	229.45	0.57	229.61	0.00	228.40	0.00
	3	230.96	0.00	235.46	0.96	230.35	0.64	233.36	0.06*	228.51	0.32
	4	235.13	0.26	241.74	0.44	238.60	0.51	233.37	0.32	229.87	0.00
	5	235.33	0.64	238.63	0.96	229.76	0.32	238.84	0.00	228.40	0.00
	6	230.74	0.64	235.09	0.95	228.68	0.23	229.84	0.33	229.20	0.00
	7	231.67	0.38	233.78	0.32	231.54	0.64	231.43	0.00	234.20	0.32
	8	227.44	0.51*	229.55	0.63*	224.74	0.00*	231.36	0.64	226.34	0.64
	Average...	231.08	8.53†	235.39	9.08	230.50	13.86	232.46	9.23	229.24	7.86
Solution B	1	127.70	0.70	137.00	0.90	128.50	0.70	133.00	0.00	128.40	0.40
	2	132.24	2.57	135.00	0.64	130.79	0.51	131.84	0.00	128.11	0.16
	3	127.56	0.71	133.39	0.96	130.53	0.34	132.52	0.70	129.92	0.00
	4	143.57‡	0.13	146.20	0.76	130.58	0.33	133.76	0.00	128.70	0.00
	5	133.79	0.52	138.74	0.32	127.21	0.98	136.39	0.00	129.45	0.32
	6	131.43	1.28	135.42	0.64*	128.05	1.30	129.98	0.00	128.80	0.30
	7	130.26	0.77	135.90	0.54	131.24	1.50	130.28	0.00	134.55	0.64
	8	127.96	2.52	128.70	1.28*	126.35	0.64	130.03	3.75	127.74	0.64
	Average...	130.14	6.58	136.29	7.50	129.16	4.89	132.23	6.41	129.46	6.81
Solution C	1	157.86	0.20	165.80	1.20	157.90	1.50	161.05	0.10	158.50	0.20
	2	161.32	1.28	164.98	0.98	162.02	0.06	162.12	0.00	158.31	0.20
	3	159.22	0.12*	162.75	0.32	162.76	2.82	162.20	1.00	159.69	0.00
	4	174.43‡	0.39	176.17‡	0.69	162.12	0.19	165.09	0.97	158.47	0.00
	5	165.32	0.24	167.44	0.64*	157.63	0.32	166.80	0.64	160.98	0.32
	6	161.26	1.03	164.55	0.64	158.03	1.59	159.58	0.45	158.78	0.00
	7	162.15	0.38	166.45	0.00	161.65	0.96	161.39	0.45	164.53	0.00
	8	156.92	0.77	158.79	0.00	153.25	1.29	160.29	0.92	157.84	0.64
	Average..	160.58	8.40	164.39	8.65	159.42	9.51	162.32	7.22	159.64	6.69

[1] *J. Ind. Eng. Chem.*, 1922, **14**: 429.

Collaborative results on the analysis of ammonium citrate solutions—Continued.

AMMONIA (grams per liter).

Analyst		Method I		Method II		Method III		Method IV	
		grams	diff.	grams	diff.	grams	diff.	grams	diff.
Solution A	1	53.88	0.05	53.65	0.55	53.90	0.00	52.87	0.25
	2	52.38	0.04	52.73	0.50	52.88	0.00	53.50	0.19
	3	52.72	0.33	52.38	0.51	53.29	0.00	53.23	0.09
	4	53.62	0.04	53.35	0.18	53.30	0.09	53.54	0.00
	5	54.55‡	0.20	55.25‡	0.09	55.31‡	0.08	54.73‡	0.08
	6	53.51	0.14	53.44	0.43	53.80	0.26	53.51	0.09
	7	53.86	0.07	52.27	0.77	53.18	0.51	53.83	0.17
	8	53.47	0.07	53.36	0.34	53.83	0.00	53.94	0.17
	Average..	53.35	1.50†	53.07	1.38	53.45	1.02	53.49	1.07
Solution B	1	34.26	0.28	33.96	1.18	34.37	0.05	33.95	0.10
	2	33.45	0.49	33.16	0.51	33.60	0.19	33.45	0.00
	3	33.52	0.34	33.44	0.09	33.52	0.09	33.40	0.32
	4	34.16	0.13	33.87	0.10	34.23	0.18	33.77	0.21
	5	34.80	0.08	35.14‡	0.07	35.49‡	0.09	34.28	0.08
	6	34.09	0.03	34.41	0.34	34.41	0.00	33.90	0.00
	7	34.18	0.27	33.05	0.59	33.39	0.34	34.28	0.08
	8	34.00	0.14	34.13	0.17	34.24	0.00	34.24	0.00
	Average..	34.06	1.35	33.72	1.36	33.97	1.02	34.16	0.88
Solution C	1	42.74	0.31	41.56	1.20	42.33	0.18	42.23	0.10
	2	41.90	0.38	41.86	0.00	42.35	0.00	39.22‡	0.18
	3	41.99	0.10	41.53	0.33	42.42	0.17	41.81	0.26
	4	42.50	0.21	41.84	0.07	42.35	0.04	42.43	0.32
	5	43.45‡	0.48	43.55‡	0.09	43.41‡	1.36	42.64	0.08
	6	42.27	0.10	42.53	0.09	42.48	0.17	42.29	0.14
	7	42.26	0.18	41.85	0.34	41.99	0.17	42.50	0.17
	8	42.36	0.06	42.59	0.00	42.50	0.17	42.59	0.00
	Average...	42.29	0.84	41.97	1.06	42.35	0.51	42.36	0.83

*Average of two determinations only.
†Maximum difference in grams by different analysts
‡Omitted from average.

by physical-chemical methods involving no analytical procedure, to have the composition of a solution of triammonium citrate in which the ratio of ammonia to citric acid should theoretically be 1:3.759. The figures obtained by Methods III and V approach this ratio much more closely than those secured by any other method, being 1:3.763 and 1:3.766, respectively, using the average values for ammonia obtained by Methods III and IV.

THE COMPOSITION OF A NEUTRAL SOLUTION OF AMMONIUM CITRATE.

In last year's report the writer recommended "that a neutral solution of ammonium citrate be considered as one in which the ratio of

ammonia to anhydrous citric acid is as 1:3.794±0.02, etc." The selection of this figure was based upon the analyses of several carefully neutralized solutions by the formaldehyde titration method, *i. e.*, Method V of the present report. These solutions were prepared in small quantities and with great care. Solution B used in this year's work was prepared by the colorimetric method, recommended last year, and amounted to about twelve liters. It is interesting to note that the ratio of ammonia to citric acid in this solution determined from the average figure obtained by Methods III and V for citric acid and III and IV for ammonia, representing the average of nearly fifty determinations is 1:3.795. The limits of agreement with this value greatly exceed those permitted by the recommendation, varying from 1:3.708 to 1:3.949 when the extreme average values are used. Although the usual variation was much lower than this it still embraces a range greater than the recommended one[1]. The direct determination of the reaction appears, therefore, to be much more accurate as well as more simple than the indirect one of determining the composition of the solution. In view of this fact the associate referee favors eliminating from the original recommendation the alternative method of adjusting the reaction by analysis.

RECOMMENDATIONS.

It is recommended—

(1) That a neutral solution of ammonium citrate be considered as one having a reaction corresponding to a pH of 7.0±0.2.

(2) That that section of the official methods dealing with the preparation of neutral solutions of ammonium citrate[2] be changed to read as follows:

REAGENTS.

In addition to the reagents described under **4** and **7** prepare ammonium citrate solutions by the following method:

Ammonium citrate solution.—For every liter of solution required dissolve 172.00 grams of anhydrous or 188.13 grams of crystallized citric acid in approximately 700 cc. of water; nearly neutralize with ammonium hydroxide; cool; measure the volume of the solution or make it up to a convenient volume, taking care to keep the density above 1.09; make exactly neutral, testing as follows:

With a pipet transfer 5 cc. of the citrate solution to a test tube (7x⅞ inches is a convenient size) and dilute to 20 cc. with distilled water. Add from a dropping bottle 5 drops of a solution of phenol red indicator (0.08%), either an alcoholic solution of the dye or an aqueous solution of its alkali salt being suitable. From a buret run in dilute ammonia solution until the color approximates that of a standard buffer solution having a pH of 7.0 contained in a similar test tube and with the same concentration of indicator. (This solution may be prepared by mixing 50 cc. of 0.2M dihydrogen potassium phosphate solution and 29.63 cc. of 0.2N sodium hydroxide solution and making up

---

[1] The writer is investigating the causes for these errors and will report the results in a paper supplementing this report.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 4.

to 200 cc., as recommended by Clark & Lubs[1]. Chemicals, especially purified for this purpose, which can be procured from several supply houses, should be used and the standard solution finally used should not have stood more than a few days unless some means of checking its reaction are available.) Complete the process by adding the dilute ammonia solution in small amounts and comparing the colors in a comparator[2]. From the amount of ammonia solution required to produce in the sample a color which exactly matches that of the standard, calculate the amount required to neutralize the rest of the solution.

Add this calculated quantity of ammonia to the original solution and check its reaction against that of the neutral standard, using the technique described above. If the colors match dilute the solution to a density of 1.09 at 20°C.

REPORT ON NITROGEN.

By I. K. Phelps (Bureau of Chemistry, Washington, D. C.), *Associate Referee on Nitrogen in Fertilizers.*

The instructions sent to collaborators for the study of the Devarda alloy method varied slightly from those sent out last year[3]. To the list of reagents was added sodium hydroxide solution—specific gravity 1.453 (42 per cent by weight). No change was made in the directions headed *Determination.* Under the heading *Experiments*, Series I, the time was changed so that in (A) 1 hour was used, (B) 1¼ hours, and in (C) 1½ hours; in Series II, 5 grams of potassium nitrate were used in place of 4 grams. Series III was not changed; Series IV was changed completely, the following directions being sent:

IV.—Repeat the series of experiments omitting the blanks, using the sample of sodium nitrate. Retain solution of potassium and sodium nitrate for comparison of results with the modified Kjeldahl-Gunning-Arnold method by H. C. Moore[4].

The following directions were sent for the study of the Moore method:

REAGENTS.

(a) *Salicyl-sulfonic acid.*—40 grams of salicylic acid are made up to 1 liter with concentrated sulfuric acid.

(b) *Sodium thiosulfate (hyposulfite) (hypo).*—Commercial photographic, pea size.

(c) *Potassium or sodium sulfate.*—Preferably dry powder.

(d) *Mercuric oxide.*

(e) *Caustic soda.*—Dissolve 30 pounds of commercial caustic soda in about 2.5 gallons of water, let settle, and siphon off the clear solution. This strong caustic soda is practically free from carbonate.

(f) *Sodium sulfide.*—Dissolve 100 grams of fused sodium sulfide in water and dilute to 1000 cc.

(g) *Pure granulated, or 20-or 30-mesh zinc.*—Pure zinc is essential as impure zinc reacts so actively with the sodium hydroxide that the rapid evolution of hydrogen

---

[1] *J. Bact.*, 1917, 2: 26; W. M. Clarke. The Determination of Hydrogen Ions, (Baltimore), 76.
[2] One made from a block of wood as described by Dernby and Avery, *J. Exp. Med.*, 1918, 28: 348, serves the purpose very well and can be made by any carpenter.
[3] *J. Assoc. Official Agr. Chemists*, 1922, 5: 451.
[4] *J. Ind. Eng. Chem.*, 1920, 12: 669.

carries over by entrainment some free alkali, even when using the Hopkins connecting bulb. This causes a variable blank. The Davisson bulb will prevent this entrainment.

(h) *0.5N sulfuric acid solution.*

(i) *0.2N or 0.1N sodium hydroxide solution.*

(j) *Sodium alizarin sulfonate.*—2 grams in 100 cc. of water.

DETERMINATION.

Transfer 0.5 gram $NaNO_3$, or KNO_3 preferably, to a 650 cc. Pyrex Kjeldahl flask; add 35 cc. salicyl-sulfonic acid, preferably from a dispensing buret, rinsing down the neck of the flask; warm over low heat or in boiling water or steam bath until reaction begins, shaking frequently until solution is complete; add 5 grams hypo, heat over low heat until frothing ceases (about 5 minutes), then add 10 grams sodium or potassium sulfate, 1 gram mercury, and continue digestion until clear, and for one hour afterwards, boiling briskly; cool; dilute with water to about 400 cc.; add a small pinch of 20-or 30-mesh zinc (0.1 gram), and 70 to 80 cc. caustic soda in which are dissolved 2 grams fused sodium sulfide. Sulfide may be added previous to adding the zinc and NaOH. The ammonia is distilled and collected in 0.5N sulfuric or hydrochloric acid. About 200 to 250 cc. distillates are sufficient, requiring about ½ to ¾ hour. Use in receiving flask a sufficient quantity of 0.5N acid diluted to 75 to 100 cc. with distilled water and three drops of sodium alizarin sulfonate.

Alternate indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperatures. Five cc. of the filtered solution is employed as an indicator. This cochineal solution will keep in good condition for use for about two weeks only.

DIRECTIONS FOR EXPERIMENTS COMPARING H. C. MOORE'S METHOD WITH THE DEVARDA ALLOY METHOD.

Blanks I.—Prepare your reagents and conduct 5 determinations of the nitrogen in the reagents used, following the directions given. Record the results in Series I as obtained. (Do not round off the figures, or give averages.)

Series II.—Accurately transfer by means of the same pipet used in the Devarda alloy work (see Series II under directions for Devarda Alloy Experiments) 25 cc. portions of the potassium nitrate solution used in the experiments using a 650 cc. Kjeldahl flask; place the flask on a steam or hot water bath and evaporate to *dryness*, and proceed according to the directions.

Series III.—Treat the solution of Series III, Devarda alloy method, exactly as Series II above.

Series IV.—Repeat Series III, above, except that the mercury is to be precipitated in these experiments with 2 grams of sodium thiosulfate, $Na_2S_2O_3+5H_2O$, dissolved in 25 cc. of distilled water.

Series IV-A.—Accurately weigh by difference in a glass-stoppered phial, approximately 0.5 gram of nitrate and transfer to 650 cc. Kjeldahl flask and proceed according to the directions given for the Moore Method.

Series V.—Repeat Series II, III, IV, IV-A, using the sample of sodium nitrate and record all results.

SUGGESTIONS.

It is recommended that the digestion be carried out over a free flame (not a luminous flame). When adding the solution of sodium hydroxide,

it should be allowed to run down the side of the flask so that it collects beneath the solution already present and is not mixed until the flask is connected with the condenser when the flask is shaken. Collect the distillate in a flask containing a measured quantity of standard acid (hydrochloric or sulfuric), and a sufficient quantity of distilled water to bring the solution above the glass end of the condenser, using an adapter, fitted gas tight to the end of the condenser, if desired. The Davisson scrubber is recommended for the connecting bulb for these determinations. When other forms of connecting bulb are used or any modification of the directions given, no matter how slight, please state in your reply. Record all results.

It has been the experience of the Nitrogen Laboratory of this Bureau that when free sulfur is present in a Kjeldahl distillation of ammonia, sodium alizarin sulfonate and methyl red are troublesome indicators but this is not observed with cochineal. If cochineal, however, is used, the standard acid and alkali solutions should be restandardized, using cochineal as an indicator, as in the actual determination of nitrogen.

The collaborators were as follows:

1. L. D. Haigh, University of Missouri, Columbia, Mo.
2. W. D. Richardson, Swift & Co., Chicago, Ill.
3. J. O. Clarke, Bureau of Chemistry, Savannah, Ga.
4. B. F. Robertson, Clemson Agricultural College, Clemson College, S. C.
5. Paul Rudnick, Armour and Co., Chicago, Ill.
6. Roy E. Neidig, University of Idaho, Moscow, Idaho.
7. G. A. Hopper, N. D. Agricultural College, Agricultural College, N. D.
8. G. J. Noggle, Jarecki Chemical Co., Sandusky, Ohio.
9. C. D. Garby, Fixed Nitrogen Research Laboratory, Washington, D. C.
10. A. O. Olsen, Dairy & Feed Commission, St. Paul, Minn.
11. R. D. Caldwell, Armour Fertilizer Works, Atlanta, Ga.
12. J. J. Vollertsen, Morris & Company, Chicago, Ill.
13. C. M. Bible, Read Phosphate Co., Nashville, Tenn.
14. J. W. Kellogg, Department of Agriculture, Harrisburg, Pa.
15. A. J. Patten, Agricultural College, E. Lansing, Mich.
16. L. F. Schmelzer, Armour Fertilizer Works, Chicago, Ill.
17. J. H. Pelot, Picatinny Arsenal, Dover, N. J.
18. W. R. Austin, Tennessee Chemical Co., Nashville, Tenn.
19. A. L. Prince, Experiment Station, New Brunswick, N. J.
20. F. B. Carpenter, Virginia-Carolina Chemical Co., Richmond, Va.
21. W. F. Hand, Mississippi Agricultural and Mechanical College, Agricultural College, Miss.
22. J. G. Smith, Bureau of Soils, Washington, D. C.
23. J. F. Ellis, Bureau of Chemistry, Washington, D. C.

Tables 1, 2 and 3 give the results obtained by the collaborators and Table 4 gives a summary of these results.

TABLE

Collaborative results on potassium nitrate

SERIES II (0.25 gram).

(Expressed as per

COLLABORATORS	1 HOUR			1¼ HOURS			1½ HOURS		
	Highest	Lowest	Average	Highest	Lowest	Average	Highest	Lowest	Average
1	13.72	13.58	13.65	13.81	13.81	13.81	13.77	13.56	13.66
2	13.80	13.72	13.77	13.83	13.81	13.82	13.77	13.74	13.76
3	13.59	13.46	13.55	13.58	13.58	13.58	13.63	13.57	13.61
4	13.82	13.75	13.77	13.85	13.82	13.83	13.82	13.75	13.80
5	13.82	13.81	13.82	13.81	13.72	13.77	13.83	13.80	13.82
6	13.78	13.75	13.77	13.71	13.71	13.71	13.77	13.75	13.76
7	13.84	13.72	13.76	13.84	13.72	13.78	13.76	13.72	13.75
8	13.82	13.66	13.77	13.82	13.66	13.77	13.82	13.62	13.75
9	13.77	13.72	13.75	13.85	13.82	13.84	13.79	13.75	13.76
10	13.40	13.20	13.33	13.40	13.04	13.28	13.60	13.44	13.52
11	13.52	13.52	13.52	13.64	13.20	13.41	13.59	13.51	13.54
12	13.93	13.73	13.81	13.97	13.69	13.86	13.97	13.88	13.93
13	13.71	13.51	13.64	13.66	13.62	13.65	13.66	13.36	13.52
14	13.65	13.53	13.60	13.65	13.41	13.52	13.53	13.41	13.46
15	13.64	13.60	13.61	13.72	13.64	13.67	13.76	13.64	13.71
16	13.76	13.74	13.75	13.71	13.69	13.70	13.80	13.79	13.80
17	13.75	13.17	13.45	13.86	12.41	13.35	13.88	13.62	13.80
18	13.64	13.60	13.63	13.72	13.68	13.71	13.72	13.68	13.69
19	13.75	13.73	13.74	13.80	13.77	13.79	13.71	13.69	13.70
20	13.49	13.32	13.43	13.55	13.48	13.51	13.60	13.49	13.53
21	13.93	13.72	13.84	13.93	13.72	13.86	13.86	13.72	13.81
22	13.87	13.87	13.87	13.87	13.71	13.80	13.87	13.82	13.85
23	13.81	13.81	13.81	13.81	13.80	13.81	13.84	13.66	13.74

TABLE

Collaborative results on sodium nitrate

SERIES II (0.25 gram).

(Expressed as per

COLLABORATORS	1 HOUR			1¼ HOURS			1½ HOURS		
	Highest	Lowest	Average	Highest	Lowest	Average	Highest	Lowest	Average
1	16.33	16.27	16.31	16.34	16.27	16.33	16.23	16.19	16.22
2	16.43	16.38	16.40	16.44	16.40	16.40	16.42	16.35	16.38
3	16.21	16.21	16.21	16.28	16.16	16.24	16.20	16.20	16.20
4	16.45	16.32	16.36	16.51	16.32	16.43	16.45	16.32	16.41
5	16.60	16.47	16.53	16.41	16.37	16.40	16.52	16.44	16.47
6	16.58	16.50	16.55	16.50	16.42	16.47	16.55	16.46	16.50
7	16.48	16.36	16.41	16.44	16.40	16.41	16.56	16.36	16.43
8	16.35	16.29	16.33	16.45	16.29	16.33	16.45	16.39	16.43
9	16.36	16.31	16.34	16.39	16.22	16.32	16.39	16.35	16.37
10	16.20	16.00	16.09	16.08	15.76	15.95	16.20	16.20	16.20
11	16.24	16.20	16.23	16.32	16.20	16.26	16.23	16.07	16.16
12	16.67	16.60	16.64	16.60	16.57	16.58	16.60	16.51	16.56
13	16.30	16.18	16.19	16.28	16.04	16.15	16.28	16.04	16.19
14	16.11	16.01	16.05	16.27	16.17	16.23	16.21	16.11	16.15
15	16.32	16.28	16.29	16.24	16.24	16.24	16.56	16.28	16.37
16	16.38	16.34	16.35	16.39	16.36	16.37	16.44	16.41	16.43
17	16.47	15.50	16.06	16.43	16.29	16.38	16.53	14.65	15.82
18	16.48	16.28	16.40	16.44	16.28	16.39	16.44	16.32	16.36
19	16.30	16.23	16.27	16.44	16.38	16.41	16.38	16.36	16.37
20	16.18	15.96	16.05	16.28	16.07	16.20	16.40	16.20	16.31
21	16.42	16.31	16.38	16.42	16.31	16.37	16.42	16.42	16.42
22	16.48	16.48	16.48	16.54	16.20	16.33	16.51	16.36	16.41
23	16.44	16.33	16.38	16.45	16.37	16.42	16.49	16.43	16.46

1.
by the Devarda method.
cent of nitrogen.)

SERIES III (0.50 gram).

1 Hour			1¼ Hours			1½ Hours		
Highest	Lowest	Average	Highest	Lowest	Average	Highest	Lowest	Average
13.79	13.70	13.76	13.79	13.75	13.78	13.74	13.70	13.72
13.83	13.82	13.82	13.84	13.83	13.83	13.83	13.81	13.82
13.37	13.36	13.36	13.51	13.46	13.48	13.51	13.42	13.47
13.85	13.75	13.81	13.85	13.82	13.83	13.82	13.78	13.81
13.91	13.87	13.89	13.83	13.80	13.81	13.86	13.84	13.85
13.90	13.84	13.86	13.90	13.83	13.86	13.91	13.88	13.86
13.86	13.86	13.86	13.82	13.74	13.78	13.92	13.78	13.83
13.77	13.66	13.72	13.82	13.71	13.78	13.82	13.82	13.82
13.81	13.80	13.81	13.81	13.77	13.79	13.82	13.74	13.79
13.54	13.42	13.48	13.52	13.42	13.47	13.48	13.38	13.44
13.70	13.66	13.69	13.70	13.64	13.68	13.59	13.49	13.55
13.91	13.63	13.80	13.94	13.92	13.93	13.94	13.91	13.93
13.77	13.61	13.75	13.68	13.60	13.65	13.72	13.66	13.68
13.80	13.66	13.71	13.80	13.72	13.78	13.77	13.65	13.72
13.74	13.62	13.67	13.74	13.56	13.67	13.76	13.68	13.69
13.78	13.74	13.76	13.81	13.79	13.80	13.80	13.75	13.77
14.18	13.71	13.94	13.96	13.76	13.86	13.92	13.65	13.76
13.66	13.66	13.66	13.70	13.68	13.69	13.70	13.64	13.67
13.66	13.64	13.65	13.85	13.82	13.84	13.83	13.82	13.83
13.70	13.60	13.65	13.50	13.48	13.53	....	....	....
13.76	13.72	13.73	13.65	13.62	13.63	13.76	13.76	13.76
13.82	13.82	13.82	13.82	13.68	13.77	13.82	13.70	13.77
13.84	13.80	13.82	13.85	13.82	13.82	13.83	13.80	13.82

2.
by the Devarda method.
cent of nitrogen.)

SERIES III (0.50 gram).

1 Hour			1¼ Hours			1½ Hours		
Highest	Lowest	Average	Highest	Lowest	Average	Highest	Lowest	Average
16.38	16.35	16.37	16.40	16.34	16.37	16.38	16.31	16.35
16.37	16.33	16.34	16.36	16.35	16.36	16.35	16.32	16.33
15.80	15.44	15.56	16.21	15.70	15.95	15.61	15.36	15.53
16.42	16.32	16.37	16.42	16.38	16.39	16.45	16.42	16.43
16.48	16.43	16.46	16.51	16.44	16.48	16.44	16.41	16.42
16.56	16.42	16.48	16.54	16.40	16.49	16.53	16.50	16.51
16.46	16.40	16.42	16.40	16.36	16.39	16.48	16.36	16.41
16.42	16.37	16.40	16.46	16.37	16.43	16.42	16.37	16.40
16.40	16.39	16.40	16.38	16.30	16.35	16.41	16.31	16.37
16.12	16.06	16.10	16.40	15.96	16.16	16.12	16.12	16.12
16.36	16.28	16.31	16.32	16.10	16.23	16.21	16.19	16.20
16.75	16.61	16.67	16.69	16.61	16.66	16.67	16.55	16.62
16.33	16.23	16.26	16.26	16.08	16.14	16.34	16.08	16.17
16.46	16.32	16.41	16.50	16.30	16.43	16.41	16.35	16.38
16.34	16.32	16.33	16.28	15.92	16.15	16.28	16.28	16.28
16.50	16.46	16.48	16.47	16.44	16.46	16.44	16.41	16.43
16.44	16.22	16.33	16.34	16.30	16.31	16.35	15.89	16.11
16.34	16.32	16.33	16.36	16.32	16.35	16.40	16.36	16.38
16.43	16.40	16.42	16.46	16.42	16.44	16.46	16.44	16.45
16.35	16.24	16.30	16.40	16.28	16.33	....	....	....
16.45	16.21	16.31	16.38	16.34	16.36	16.31	16.31	16.31
16.54	16.40	16.45	16.55	16.40	16.45	16.50	16.35	16.43
16.42	16.35	16.38	16.48	16.44	16.47	16.44	16.39	16.42

TABLE

Collaborative results by the

SODIUM NITRATE.

(Expressed as per

COLLABORATORS	Series II			Series III			Series IV			Series IV-a		
	Highest	Lowest	Average	Highest	Lowest	Average	Highest	Lowest	Average	Highest	Lowest	Average
1	16.33	16.31	16.32	16.34	16.16	16.22	16.31	16.22	16.25	16.38	16.33	16.35
2	16.16	16.11	16.14	16.18	16.04	16.11	16.34	16.03	16.35	16.38	16.13	16.27
3	16.28	16.00	16.20	16.34	16.18	16.27	16.31	15.63	16.05	.....	.....	.....
4	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
5	16.49	16.08	16.33	16.67	15.66	16.42	.....	.....	.....	16.71	15.50	16.31
6	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
7	16.32	16.00	16.20	16.36	16.24	16.34	16.44	15.98	16.37	16.32	14.44	16.00
8	16.47	15.98	16.24	16.38	16.05	16.27	16.41	16.27	16.40	16.60	16.26	16.43
9	16.38	16.24	16.31	16.39	16.20	16.33	16.38	15.68	16.19	16.27	16.10	16.26
10	16.28	15.52	15.93	16.34	15.66	16.02	16.20	15.73	16.00	16.63	15.77	16.05
11	16.40	16.20	16.28	16.28	16.24	16.27	16.38	16.30	16.35	16.32	16.26	16.29
12	16.73	16.25	16.55	16.66	15.51	16.13	16.13	16.42	15.78	.....	.....	.....
13	16.48	16.04	16.23	16.24	16.08	16.17	16.24	16.06	16.15	16.29	16.21	16.25
14	16.34	16.26	16.29	16.41	16.21	16.30	16.39	16.19	16.30	16.31	16.25	16.28
15	16.20	15.52	15.86	16.26	16.08	16.17	.....	.....	.....	16.28	16.12	16.20
16	16.41	16.27	16.32	16.42	16.36	16.38	16.43	16.37	16.40	16.33	16.14	16.19
17	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
18	16.43	16.28	16.36	16.38	16.32	16.35	16.44	16.40	16.43	16.38	16.34	16.35
19	16.28	13.32	15.60	12.33	11.61	11.87	13.69	10.04	11.57	.....	.....	.....
20	16.32	16.28	16.30	.....	.....	.....	.....	.....	.....	.....	.....	.....
21	16.91	16.66	16.68	16.59	16.49	16.53	.....	.....	.....	16.70	16.49	16.58
22	16.29	16.18	16.23	.....	.....	.....	.....	.....	.....	.....	.....	.....
23	16.35	16.29	16.31	16.40	16.05	16.34	16.42	16.29	16.35	16.52	15.41	16.28

TABLE 4.

Summary of collaborative results.

(Expressed as per cent of nitrogen.)

DEVARDA METHOD.

		Series II			Series III		
		1 Hr.	1¼ Hr.	1½ Hr.	1 Hr.	1¼ Hr.	1½ Hr.
1. Total average..........	KNO_3.	13.66	13.68	13.69	13.73	13.74	13.74
	$NaNO_3$	16.30	16.33	16.32	16.34	16.35	16.32
2. Average of results when scrubber was used.....	KNO_3.	13.65	13.65	13.69	13.73	13.74	13.73
	$NaNO_3$	16.29	16.31	16.31	16.33	16.34	16.30
3. Average of (2) omitting results of Collaborators 3 and 10............	KNO_3.	13.68	13.68	13.71	13.75	13.76	13.75
	$NaNO_3$	16.33	16.35	16.34	16.39	16.38	16.37

H. C. MOORE METHOD.

		Series II	Series III	Series IV	Series IVa
Total average..................	KNO_3..	13.57	13.68	13.67	13.71
	$NaNO_3$.	16.23	16.03	15.93	16.28
Average, omitting results of Collaborator 10................	KNO_3..	13.61	13.70	13.68	13.72
	$NaNO_3$.	16.25	16.03	15.93	16.30

3.
H. C. Moore method.

POTASSIUM NITRATE.

cent of nitrogen.)

Series II			Series III			Series IV			Series IV-a		
Highest	Lowest	Average	Highest	Lowest	Average	Highest	Lowest	Average	Highest	Lowest	Average
13.75	13.56	13.68	13.84	13.79	13.81	13.82	13.80	13.81	13.83	13.18	13.82
13.72	13.53	13.64	13.71	13.57	13.62	13.84	13.49	13.70	13.70	13.60	13.64
13.59	12.85	13.44	13.89	13.46	13.66	13.76	13.60	13.69	......	..	. ....
.....	.....	.....	......	......	......	......	.....	......	.....	.....	.....
13.71	13.04	13.44	13.87	13.69	13.78	... .	. .	...	13.99	13.21	13.77
.....	.....	....	13.89	13.80	13.84	13.86	13.77	13.83	......	.....	......
13.84	13.44	13.60	13.82	13.66	13.74	14.00	13.74	13.90	13.83	13.54	13.68
13.84	13.34	13.60	13.90	13.34	13.68	13.86	13.53	13.73	14.13	13.64	13.85
13.81	13.67	13.72	13.78	13.56	13.69	13.88	13.63	13.80	13.74	13.55	13.68
13.72	11.92	12.76	13.62	12.90	13.33	13.70	13.24	13.50	13.82	13.42	13.63
13.64	13.56	13.59	13.70	13.60	13.65	13.78	13.72	13.75	13.70	13.66	13.69
13.93	13.81	13.88	13.97	13.35	13.68	13.42	11.52	12.56	......	..	.
13.66	13.50	13.58	13.76	13.66	13.71	13.78	13.56	13.71	13.71	13.50	13.65
13.62	13.54	13.58	13.31	13.19	13.26	13.75	13.73	13.74	13.80	13.77	13.79
13.60	13.20	13.40	13.68	13.60	13.64	..... .	.. ..	.. ..	13.62	13.16	13.39
13.88	13.78	13.83	13.79	13.67	13.75	13.87	13.70	13.76	13.84	13.60	13.67
.....	.....	....	.....	... .	......	......	.....	......	.....	....	...
13.72	13.64	13.67	13.70	13.68	13.69	13.76	13.68	13.77	13.78	13.72	13.75
12.99	12.69	12.79	13.71	13.28	13.42	13.72	13.37	13.55	.. ...	.	...
13.76	13.70	13.73	......	......	......	.....	.....	.....	......	...	....
14.28	13.79	14.08	13.97	13.83	13.91	... ..	.	.. .	14.00	13.90	13.94
14.10	13.56	13.83	13.79	13.76	13.77	13.71	13.59	13.64	. ... .	......	. .
13.83	13.75	13.79	13.83	13.55	13.77	13.87	13.39	13.77	13.97	13.61	13.76

DISCUSSION.

Devarda method.—Under the conditions specified, including the amounts of nitrate and the forms of apparatus, it is concluded that an hour is sufficient time for distillation. An extension of the time of distillation to one hour and a half does not appear to give any positively detectable difference. This conclusion agrees with the collaborative results of a year ago in that it indicates that an hour is sufficient time.

Those collaborators using the Davisson scrubber obtain results slightly higher and nearer the theoretical figure than those using other forms of apparatus.

The H. C. Moore method.—The results for sodium and potassium nitrates using 0.25 and 0.5 gram, respectively, are contradictory, the sodium nitrate giving lower results consistently with 0.5 gram and the potassium nitrate giving higher results. The substitution of sodium thiosulfate as a precipitant for mercury apparently gives slightly lower results. It is doubted if the differences noted above are proved to be due to the differences in experimentation noted. The comparison of the results for the dry nitrates and for the nitrates in solution is the most striking of all the comparisons here made and is believed to be significant. Sodium nitrate gives decidedly higher results for the dry

salt. Since this salt is hydroscopic, the inference is drawn that the freedom from water or, in other words, the concentration of the sulfuric-salicylic acid mixture is a critical condition in determining the completeness of the reduction of the nitrate. It is thought that this conclusion should be further studied with collaborators next year. It is possible that the apparent differences mentioned above for sodium and potassium nitrates in 0.25 and 0.5 gram amounts, and also for thiosulfate in place of sulfide may, in fact, be due to adventitious differences in the concentration of the sulfuric-salicylic acid mixture. Certainly the results obtained by the collaborators show too wide differences to be entirely satisfactory. If, however, the method can be made to give more exact and dependable results, it can be recommended for use. The technique of the method is so similar to that of the Kjeldahl method that it appears to be worthy of further study.

Sodium thiosulfate as a precipitate for mercury in the Kjeldahl method.—Commercial sodium and potassium sulfides are satisfactory in pure condition for precipitants for mercury in the Kjeldahl method. They also possess the advantage of cheapness. However, the impurity in which they are commonly found and their tendency to oxidation present conditions which are unfavorable to their use. Sodium thiosulfate, on the other hand, is reasonably cheap and presents the advantage of being relatively stable, both as a salt and in solution.

RECOMMENDATIONS.

It is recommended—

(1) That the referee for 1923 be instructed to study the Devarda method as applied to the nitrates of commerce, as it is believed that the collaborative work on pure nitrates has shown with sufficient definiteness the conditions which should be used.

(2) That the Moore method for nitrates be studied with collaborators next year.

(3) That the Referee on Nitrogen for 1923 be instructed to study the use of sodium thiosulfate as a substitute for sodium or potassium sulfide in precipitating mercury in the Kjeldahl method.

REPORT ON POTASH.

DEVELOPMENT OF THE LINDO-GLADDING METHOD AND INVESTIGATION OF OTHER METHODS FOR POTASH DETERMINATION BY THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

By J. T. Foy (Clemson Agricultural College, Clemson College, S. C.), *Associate Referee*.

It has long been known that the official Lindo-Gladding method does not account for 100 per cent of the water-soluble potash, or for all the potash probably available as plant food, especially in mixtures of acid phosphate and potash. A method or process which will account for all of this potash will be welcomed by all, and for the benefit of those who may further investigate it is believed that a review of the proceedings of the A. O. A. C. in reference to investigations of methods for the determination of potash in mixed fertilizers will be helpful. This report will necessarily be largely a history of the Lindo-Gladding method, with the changes made since it was brought before the association in 1886.

The first official method adopted corresponds closely with the present optional method with the following exceptions: hydrochloric acid was employed along with water in effecting the solution of potash; no oxalic acid or ammonium oxalate was employed in the precipitation of the lime; and two separate treatments with ammonium carbonate, accompanied by an additional filtration, evaporation and ignition[1] were necessary.

In 1885, H. W. Wiley reported the results of cooperative work carried out under his direction and as a result the use of hydrochloric acid as a solvent was discontinued.

The Lindo-Gladding method was compared with the official method in 1886, and proving quite satisfactory it was used as an alternate method. It was adopted as official in 1887, the former official method being made an alternate method.

The association carried on the work of improving the official method from year to year. A few minor changes were made, such as adding ammonia to the solution before adding ammonium oxalate, and omitting the use of sodium chloride just before the addition of platinic chloride.

The accuracy of the Lindo-Gladding method was challenged by German authorities in 1893 when they made determinations by the Stassfurt method on samples of mixed fertilizers forwarded by the association, claiming that the sulfuric acid, both free and combined, was responsible for a considerable share of the assumed errors. In the

[1] U. S. Div. Chem. Bull. 57: 58.

Stassfurt method the sulfates were removed and the solution was made with weak acid, the method as a whole not being applicable to mixed fertilizers.

In 1893, N. Robinson[1] found that noticeable losses of potash were shown by the official method. The chief source of error arose from the occlusion of potash salts by the heavy precipitates formed by addition of ammonia and ammonium oxalate, or to some potash forming an insoluble compound with silica or other substance present. Small losses were attributed to the alcohol washings and to the solvent action of ammonium chloride solution on the precipitate. Few analytical methods give a precipitate absolutely insoluble in the wash liquid.

The present method for potash salts was adopted in 1897; this method called for direct evaporation of the water solution without addition of ammonia or ammonia oxalate.

The failure of the Lindo-Gladding method to obtain all the potash soluble in water, especially from mixtures of acid phosphate and potash was realized and, in 1900, F. B. Carpenter suggested that the addition of 5 to 10 grams of ammonium chloride to the weighed sample might aid in securing solution of all potash present. The association found that this did increase the potash 0.07 per cent, but the large amount of ammonia salts left after evaporation with sulfuric acid is a disadvantage, as it might cause sputtering.

The association investigated the method by C. L. Hare[2] in which "milk of lime" was substituted as the precipitant for phosphates, iron, alumina, etc., in place of ammonia and ammonium oxalate, which eliminated the evaporation to expel ammonia, thus avoiding the probable loss of potash during evaporation. This method proved to be rapid, but trouble was encountered in washing the final precipitate due to the large amount of lime, etc. When organic matter is present the sample is ignited with dilute sulfuric acid, which was an objection, especially in States that require the potash to be soluble in water. Further experiments were made in the hope of finding a method that would dissolve all the potash in mixed fertilizers. The theory was advanced that sodium salts are occluded before those of potash; consequently sodium hydrate was used instead of ammonia. This was followed by some work done by F. B. Carpenter who showed that an average of 0.3 per cent potash was occluded in the heavy precipitate formed by addition of ammonia and ammonium oxalate, and that the occlusion was not due to formation of insoluble potash compounds. It was suggested that 5 cc. of hydrochloric acid be added when making the solution, that it be neutralized with sodium hydrate, and that powdered ammonium oxalate be added. The results by this modification were very gratify-

[1] *J. Am. Chem. Soc.*, 1894, **16**: 364.
[2] U. S. Bur. Chem. Bull. 73: 38.

ing, the amount of potash found very nearly approaching the theoretical.

It was recommended that these changes be made in the official method, but, in 1905, by a vote in which chemists in charge of fertilizer control were the only qualified voters, the recommendation was lost, due principally to laws that existed in twenty-seven states which required the potash to be soluble in water. It was agreed, however, that this small amount of acid in the water solutions, while not liberating any of the insoluble forms of potash, would liberate any occluded potash in the substance which would be available to plant food. The association appointed a committee to define "available potash", but the report of this committee could not be found in the records.

The volumetric estimation of potash as phosphomolybdate, proposed by M. G. Donks, was suggested as affording a possible means of recovering all the potash in mixtures containing acid phosphate and potash. The association worked on this method and modifications of the method for three years and in 1908 recommended that further work be discontinued for the time being, in order to take up the cobalt-nitrite volumetric method, as modified by Drushel[1]. This method gave closer agreement with the official method than did the phosphomolybdate method. This work was discontinued in 1910. The gravimetric cobalt-nitrite method was also tried out.

In 1908 the use of ammonia and ammonium oxalate was employed in the determination of potash salts. Lower results were reported, which tended to prove the contention of some that potash is occluded in the precipitate formed.

One of the most important changes made was the adoption of Breckenridge's[2] modification of the official method in 1912, which provided for the washing of a weighed amount of sample through filter paper with hot water to a volume of about 200 cc. and in case of mixed fertilizers, adding 2 cc. of hydrochloric acid and heating to boiling, ammonia and ammonium oxalate being added and potash determined in the usual way. In 1917 the addition of 2 cc. of hydrochloric acid was eliminated.

The perchlorate method was first studied in 1912 and, with various improvements and modifications, including the barium hydroxide process and the modification of the De Roode moist combustion perchloric acid method by Keitt and Shiver[3], was before the association continually until 1920.

Moore and Caldwell[4] have shown that higher results can be obtained by using stronger alcohol for the first washings in the official method, owing to a solvent effect of the 80 per cent alcohol or to the presence of sodium salts in the alcoholic solution. Hazen also finds that stronger

[1] Chem. News, 1908, 97: 124.
[2] *J. Ind. Eng. Chem.*, 1909, 1: 409, 804.
[3] *Ibid.*, 1918, 10: 219; 1919, 11: 1049.
[4] *Ibid.*, 1920, 12: 1188.

(90 per cent) alcohol gives higher results[1]. Robertson and McDonnell, in 1904, found there was no material difference in results in the use of 95 per cent alcohol and 80 per cent alcohol in washing the precipitate. This question is still before the association.

The centrifugal method by Sherrill[2] is now before the association, but it is the writer's opinion that this method is not suitable as an official method. but is applicable where a quick approximate potash determination is required as in factory control.

This review shows that the Lindo-Gladding method has constantly been before the association, and such chemists as Wiley, Ross, Carpenter, Hare, Fraps, Breckenridge, Jarrell and others have contributed to its improvement and development.

It is today the best method available for potash in mixed fertilizers, and except for the loss of a small amount of potash due to occlusion, especially in mixtures of acid phosphate and potash and the probable loss due to the solubility of the precipitate in 80 per cent alcohol, it would be above criticism. The loss by occlusion is partly compensated for by the decreased volume of the supernatant liquid caused by the heavy precipitate. This error could in some cases be avoided by the addition of a small amount of hydrochloric acid to the wash water, especially in mixtures of acid phosphate and potash. This change, of course, would conflict with the existing laws in some States, which call for water-soluble potash only. If future results warrant this change, it is possible that the different State fertilizer boards of control could have those laws modified to suit the conditions.

RECOMMENDATIONS.

It is recommended—

(1) That investigation of the centrifugal method by Sherrill be discontinued.

(2) That a further study of the use of stronger alcohol for first washings of the precipitate as suggested by Moore and Caldwell be continued.

(3) That the use of weak acid in making the solution in mixtures of acid phosphate and potash be investigated.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 456.
[2] *Ibid.*, 1921, 13: 227.

SUMMARY RELATING TO STRENGTH AND KIND OF ALCOHOL USED IN OFFICIAL POTASH METHODS, 1884–1921.

By H. A. HUSTON (Soil and Crop Service of the Potash Syndicate, 42 Broadway, New York, N. Y.).

A. As printed in official or provisional methods.
B. Recommendations by reporter or referee.
C. Suggestion or comment by member of association.
D. Recommendation or comment by other chemists.

1884.

A—Atlanta Meeting, May: 95 per cent alcohol.

A—Philadelphia Meeting, September: strong alcohol (80–95 per cent), more alcohol.

1885.

A—85 per cent alcohol followed by 5 cc. of ether.

C—W. C. Stubbs[1] stated he used 95 per cent alcohol + $\frac{1}{6}$ its volume of ether.

D—T. S. Gladding[2], in the proposed Lindo-Gladding method, used for superphosphates alcohol and ammonium chloride solution, followed by chemically pure alcohol.

1886.

A—Lindo-Gladding { superphosphates—alcohol, pure alcohol.
sulfate and kainite—alcohol, alcohol.

Alternate method—strong alcohol, strong alcohol, 5 cc. of ether.

B—W. J. Gascoyne[3] recommended alternately strong alcohol, 5 cc. of ether, ammonium chloride solution, alcohol, 5 cc. of ether.

1887.

A—Lindo-Gladding { superphosphates—alcohol, pure alcohol.
sulfate and kainite—alcohol, alcohol.

Alternate—strong alcohol, strong alcohol.

1888.

A—Same as in 1887.

B—Reporter states New Jersey Station uses 80 per cent alcohol in Lindo-Gladding method.

1889.

A—Same as in 1887.

[1] U. S. Bur. Chem. Bull. 7: (1885), 25.
[2] *Ibid.*, 40.
[3] *Ibid.*, 12: (1886), 51.

1890.

A—Lindo-Gladding—same as in 1887.
Alternate—strong alcohol.

1891.

A—Lindo-Gladding—same as in 1887.
Alternate—80 per cent alcohol, strong alcohol, 5 cc. of ether.

1892.

A—Same as in 1891.

1893.

A—Same as in 1891.

1894.

A—Use of ether struck out; otherwise same as in 1891.

1895.

A—All alcohol to be 80 per cent.
B—H. J. Wheeler[1] recommended 80 per cent alcohol for all. Adopted.
C—F. P. Veitch[2] suggested one strength alcohol instead of 80 per cent and ordinary alcohol.

1896–1901.

A—80 per cent alcohol.

1902.

A—80 per cent alcohol.
D—G. W. Lehmann[3] reports comparison of 95 per cent alcohol with 80 per cent followed by ammonium chloride solution, the latter giving low results.

1903.

A—80 per cent alcohol.
C—C. C. McDonnell[4] used 95 per cent alcohol for final washing on official samples.

1904.

A—80 per cent alcohol.
C—J. W. Kellogg[5] says he had difficulty in dissolving sodium chloroplatinate (Na_2PtCl_6) in 80 per cent alcohol.

[1] U. S. Bur. Chem. Bull. 47: (1895), 23.
[2] *Ibid.*, 18.
[3] *Ibid.*, 73: (1902), 33.
[4] *Ibid.*, 81: (1903), 127.
[5] *Ibid.*, 90: (1905), 111.

1905–1910.

A—80 per cent alcohol.

1911.

No report.

1912.

A—80 per cent alcohol.

C—C. Beatty[1] compared "denatured" alcohol with ordinary alcohol. No difference.

1913.

A—80 per cent alcohol.

B—Reporter states results using "denatured alcohol commercial" are comparable with ethyl alcohol, when used in same strength, and asks for trial of it.

1914.

A—80 per cent alcohol, sp. gr. 0.8645–15/15. This is 80 per cent by *volume*. Denatured alcohol, Formula 1, may also be used after dilution with water to make 80 per cent by *volume*.

B—Recommended denatured alcohol as under A.

C—E. E. Vanatta[2] reports losses in 3 washings with 80 per cent alcohol—50 cc. portions—1.8 to 6.2 milligrams. A. L. Gibson[3] reports very little difference between 80% denatured and 80% ethyl alcohol.

1915.

A—80 per cent by volume.

C—P. L. Hibbard[4] thinks alcohol stronger than 80 per cent should be used.

1916–1919.

A—80 per cent by volume.

1920.

A—80 per cent by volume.

B—No report in proceedings.

D—Caldwell & Moore[5] presented paper on varying the strength of alcohol in Lindo-Gladding method. It would seem that the results reported, which overran the theory, might be accounted for by insufficient washing (only 3 times) before using the ammonium chloride solution.

---

[1] U. S. Bur. Chem. Bull. 162: (1913), 20.
[2] *J. Assoc. Official Agr. Chemists*, 1914, 1: 407.
[3] *Ibid.*, 404.
[4] *Ibid.*, 1917, 3: 116.
[5] *J. Ind. Eng. Chem.*, 1920, 12: 1188.

1921.

A—80 per cent by volume.

B—Recommendation of the previous year that strength of alcohol be studied, repeated.

C—William Hazen[1] compared 80, 90, and 95 per cent alcohol. Recommended that 90 per cent be used for first, and 80 per cent for final washing.

Solubility of K_2PtCl_6 in Alcohol.

Soluble in 42,500 parts absolute alcohol (Precht)[2].

Archibald, Wilcox and Buckley[3] give results of extensive experiments, from which it is seen that 100 grams of saturated solution of K_2PtCl_6 in ethyl alcohol, 70 per cent by weight, contain 0.0128 gram; 80 per cent—0.0085 gram; 90 per cent—0.0025 gram; and 100 per cent—0.0009 gram.

Peligot[4] gives 80 per cent—0.05 gram; 90 per cent—0.02 gram.

Solubility of K_2PtCl_6 and Na_2PtCl_6 in Alcohol.

Bulletin 43[5] states:

One liter of 90 per cent alcohol contains 0.03 gram K_2PtCl_6 and one liter of 60 per cent alcohol dissolves 110 grams Na_2PtCl_6; one liter 95 per cent alcohol dissolves 22 grams Na_2PtCl_6.

Precht (Comey)[6] Na_2PtCl_6 more soluble in absolute alcohol than in 95 per cent alcohol. Saturated solution in absolute alcohol contains 11.90 per cent; in 95 per cent alcohol, 6.34 per cent.

Solubility of Ammonium Chloride in Ethyl Alcohol (Comey).

One hundred parts, sp. gr. 0.872 (75.35 per cent by volume), dissolves 4.75 parts; 100 parts, sp. gr. 0.834 (88.55 per cent by volume), dissolves 1.5 parts; 100 absolute dissolves 0.62 parts at 19. Ten cc. of mixed alcohols containing 10.40 per cent methyl and 89.60 per cent ethyl alcohol dissolve 0.0658 gram of NH_4Cl.

$MgPtCl_6+6H_2O$ solution in absolute alcohol.

$BaPtCl_6+6H_2O$. Decomposed by alcohol.

$MgCl_2+6H_2O$ much more soluble in strong than in dilute alcohol.

$MgSO_4+7H_2O$ 100 parts absolute alcohol dissolve 1.3 parts at 0.

Hubbard[7] published an extended article on potash determination,

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 456.
[2] *Z. anal. Chem.*, 1879, 18: 509.
[3] *J. Am. Chem. Soc.*, 1908, 30: 747.
[4] *Ibid.*, 755.
[5] U. S. Bur. Chem. Bull. 43: (1894), 229.
[6] Comey-Hahn, a Dictionary of Chemical Solubilities—Inorganic, 2nd ed. 1921.
[7] *J. Ind. Eng. Chem.*, 1917, 9: 504.

with bibliography. He shows that K_2PtCl_6 is about four times as soluble in 80 per cent alcohol as in 95 per cent. He states that only a slight excess of platinum solution (not enough to form Na_2PtCl_6) should be used, because of the slow solubility of Na_2PtCl_6 in alcohol.

No report on potash availability was made by the associate referee.

AVAILABILITY OF POTASH IN MIXED FERTILIZERS.

By N. E. Gordon (Chemistry Department, University of Maryland, College Park, Md.).

The paper, "The Determination of Potash in Mixed Fertilizers", by F. B. Carpenter, given before the American Chemical Society at Pittsburgh, September 5–8, 1922, prompted the writer to make this report. After giving the history of the development of the potash determination in mixed fertilizers, Carpenter[1] points out the necessity of finding some method in the analysis of mixed fertilizers that will show the same amount of potash derived from the salts readily soluble in water as was employed in the formula. He says in part: "The cause of low results has never been explained, but in the investigation of the writer, a part of the potash seemed to be occluded or retained in the precipitate which results from the addition of ammonia and ammonium oxalate". He says further: "The low results in some cases may be accounted for by some slight fixation of the potash, but if such were the case, it is not strongly held and in all probability is available for plants".

No work with this particular problem in mind has been done, but the investigations on colloids during the past two years at the University of Maryland would indicate that Carpenter's assumptions are partly correct. Two points may well be discussed: (1) The cause of the low results in determining the potash in mixed fertilizers; and (2) the availability of the unrecovered potash.

THE CAUSE OF LOW RESULTS.

The low results in mixed fertilizers might be due to the colloids of ferric oxide and alumina. When the rock phosphate is treated with sulfuric acid the iron and aluminum are partially converted into soluble compounds, as can be shown by testing the filtrate in the potash determinations. At the high temperature at which this treatment is carried out these compounds rapidly undergo hydrolysis, forming gels of alumina and iron oxide; silica gel also is undoubtedly formed. The alumina and iron oxide gels act as fairly strong adsorbents for potassium salts as the following table shows:

[1] *Science*, 1922, 56: 695; *Am. Fertilizer*, 1922, 57: 55.

TABLE 1.

Adsorption of potassium from 0.1N solutions by hydrogels.

GEL USED	POTASSIUM ADSORBED PER GRAM OF GEL		
	K_2SO_4	KH_2PO_4	KNO_3
	mg.	*mg.*	
Silica	0.42	0.05	None
Alumina	9.2	74.3	None
Ferric oxide	4.0	107.2	None

It is noted that ferric oxide and alumina take up an appreciable amount of the potassium while the amount taken up by the silica may be neglected. Therefore, if either of the last two gels is present in the rock phosphate it is reasonable to suppose that a certain amount of potassium may be adsorbed.

Whether or not all this potassium can be washed out of the gel is questionable. Leaching out the phosphate has been tried, and it was found that when about six liters of water had run through, only one-half to one-third of the phosphate had been washed out, and the rate at which it was being leached at this time was almost unappreciable (0.3 milligram in 50 cc. filtrate).

TABLE 2.

Amount of phosphate radical left in the gels after washing with 6000 cc. of water.

	PO_4 IN ALUMINA GEL	PO_4 IN IRON GEL
	gram	*gram*
Before washing	0.3142	0.5788
After washing	0.2308	0.2688

The potassium in the residue was not determined, but it is believed from results of later pot experiments that it was present in a quantity equivalent to that of phosphorus.

AVAILABILITY OF UNDETERMINED POTASH.

That unrecovered potash in mixed fertilizers may be available for plant use is indicated by the following pot experiment. The hydrogels of iron and alumina were allowed to attain maximum adsorption in a solution of potassium acid phosphate. They were then subjected to leaching with water until there was scarcely any reaction obtainable in the filtrate for the phosphate radical (used because of its delicacy). Portions of the gels showed on analysis a composition similar to that given in Table 2. These gels were then mixed with sand which was free from both potassium and phosphate. Sweet potato seedlings were planted in the mixtures. After these plants had been allowed to grow

for eight weeks, they were analyzed for potassium and checked with a control plant. The gains in potassium are shown in Column 3 of Table 3. Column 4 gives the percentage of the total potassium used by the plant in eight weeks, while Column 2 gives the gain in weight.

TABLE 3.

Availability of unrecovered potash.

GEL USED	INCREASE IN WEIGHT OF PLANT	INCREASE OF POTASSIUM IN PLANT	POTASSIUM TAKEN FROM THE GEL
	per cent	*per cent*	*per cent*
Iron...............	263	129	63.3
Alumina...............	227	150	71.0

These results show that if mixed fertilizers contain colloids of ferric oxide and alumina, it is possible for the potash determinations to be low, and still for the unrecovered potash to be available for plant use.

No report on precipitated phosphates was made by the associate referee.

THE VOLUMETRIC DETERMINATION OF PHOSPHORUS[1].

By W. A. TURNER (Bureau of Animal Industry, Beltsville, Md.).

Experiments conducted to test the reliability of the Pemberton volumetric method for phosphorus have given results uniformly higher (about 8 per cent) than those obtained by the gravimetric method. These experiments were conducted on a solution of purified sodium phosphate and on samples of blood, plasma and urine. These results would correspond to a composition for ammonium phosphomolybdate such as that given by Hundeshagen[2], $(NH_4)_3\,PO_4\text{–}12\ MoO_3\text{–}2HNO_3$, and are in agreement with results obtained by recent investigators (Marchand[3], Vogel[4]). It is not thought, however, that the formula of Hundeshagen represents the true composition of the precipitate. It is thought, rather, that the precipitate consists of an acid ammonium phosphomolybdate, $(NH_4)_2\ HPO_4 \cdot 12MoO_3$ or $NH_4H_2PO_4 \cdot 12MoO_3$, together with a certain amount of occluded molybdic acid (Baxter[5]), the combined effect of which will account for the 8 per cent error observed. The error is constant and on this basis a new factor can be calculated which may be applied with very satisfactory results.

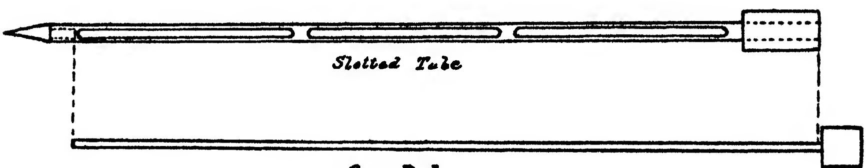
[1] Abstract of a paper presented before the meeting of the American Chemical Society in September, 1922. The complete paper will be published later in the Journal of the American Chemical Society.
[2] *Z. anal. Chem.*, 1889, 28: 141.
[3] *Chem. Abstracts*, 1919, 13: 2722; 1921, 15: 3955; *S. African J. Sci.*, 1918–19, 15: 357.
[4] *J. Soc. Chem. Ind.*, (*Trans.*), 1922, 41: 127.
[5] *Am. Chem. J.*, 1902, 28: 298; Baxter and Griffin, *Am. Chem. J.*, 1905, 34: 204.

A NEW FERTILIZER SAMPLING TUBE.

By L. D. HAIGH (University of Missouri, Columbia, Mo.).

The Association of Official Agricultural Chemists, at the meeting of November, 1919, recommended certain directions to be followed in obtaining a sample of fertilizer for analysis. Among these is the recommendation that a sampler be used which removes a core from the bag from top to bottom.

Of samplers of this type, perhaps the Indiana double-tube sampler is best known. This consists of two tubes, one inside the other. The wall on one side of the two tubes is cut away to form a long groove-like opening through which the tube is filled after insertion in the sack. By turning the inside tube to one side the opening is closed. The closed sampler is inserted into the sack; it is then opened with the openings upward. After shaking the sack to fill the tube, the sampler is closed, withdrawn, and emptied.



Recently a sampler was described by J. W. Kellogg[1] of the Pennsylvania Department of Agriculture. This sampler removes a core by boring down into the sack, the lower end being open so that the fertilizer enters as the sampler is inserted. A number of openings along the side assist in removing the sample from the tube after withdrawal. When not in use this sampler can be separated into two parts by unscrewing a joint near the center, placed in an ordinary suit case and carried from place to place. The writer has not actually worked with this sampler but from experience certain difficulties with its use might be anticipated. Among these is the probability that contents of the sack will enter at the side openings as well as at the end, both when being pushed into, and withdrawn from, the sack.

In a recent number of this *Journal*[2], the writer published a description of the sampler used in the fertilizer inspection work in Missouri, together with comparison of results of analysis of samples obtained with this sampler and with the Indiana double-tube sampler. In this article it was stated an effort was being made in Missouri to adapt the idea of the double-tube sampler to the Missouri sampler. As a result of differ-

[1] *J. Ind. Eng. Chem.*, 1922, 14: 631.
[2] *J. Assoc. Official Agr. Chemists*, 1921, 4: 597.

ent trials a new form of sampler is now in use which is free from the mechanical difficulties of the double-tube sampler and which obtains, with equal efficiency, a representative sample from the sack from top to bottom.

This new sampler consists of two parts: (1) A brass tube 30½ inches long and approximately 11-32 inches inside diameter and ½ inch outside diameter; (2) a solid brass rod fitting into the brass tube as perfectly as possible and yet sliding in and out with slight pressure.

One end of the tube is fitted with a piece of solid-brass rod ground to a point; the other end has a cylindrical wooden handle 3 inches long and 1⅜ inches in diameter. Three longitudinal slots, ¼ inch in width lying end-to-end along the tube, permit the material in the sack to enter during the operation of drawing the sample. The length of the brass tube from the end of the handle to the solid pointed end is 32 inches. The solid-brass core-rod is also provided with a handle; this is a solid-brass cylinder, 1½ inches long and 1⅜ inches in diameter. The length of the core-rod (approximately 31½ inches over all) is such that when inserted in position in the tube the lower end rests upon the solid-brass point of the brass tube, while the handle of the rod is still 1/16 inch from the handle end of the brass tube. In using the sampler the core-rod is placed in the tube; the point of the tube is then inserted into the top of the sack and the sampler, groove down, is pushed in by exerting pressure on the solid brass handle of the core-rod. If the sampler can not readily be pushed in by hand, it may be driven in by blows with a block of wood or mallet. The core-rod is now withdrawn completely from the tube without twisting, and the tube is rotated in the sack 180 degrees, or until the groove faces upwards. By tapping on the sack above the sampler the tube is readily filled with a part of the contents of the sack. The tube is now withdrawn, the operator holding a finger over the groove to push away any fertilizer which has piled upon the groove above the edges. The contents of the tube are turned out on a sheet of paper, after which the tube is held vertically and tapped a few times to remove all particles from the inside. The core-rod is now replaced and the sampler is ready for the next sack.

The contents of this tube are such that after ten sacks have been sampled the material obtained from the tube amounts to one pound or more. This is transferred to a suitable container for transportation to the laboratory.

As mentioned in the previous article, the double-tube sampler is subject to some difficulties in practice. The attempt to rotate the two tubes, one inside the other while inserted in a sack of fertilizer, causes fine material to work into the space between the tubes which at times become immovable before the sampler is opened wide. If, however, the tube opens without much difficulty, it is often impossible to close it after

filling. In the sampler just described—the center rod being withdrawn longitudinally—the fine material does not work into the space between the tube and the rod.

The experience of the writer tends to prove that with a sampler closed longitudinally it is immaterial whether the tube is closed on the side when withdrawn from the sack. If the tube has been filled before withdrawing, no more material can enter by rubbing against the side because there is no other opening from which material can be pushed out by this pressure from the sides. (This, in the writer's opinion, constitutes a serious defect in the tube described by Kellogg.) It is obvious, however, that when an open sampler is inserted into a sack, some material will enter the sampler before it is in its final position. It seems necessary, therefore, for best results, that the sampler be closed when inserted. This suggests at once that the double-tube sampler may be altered by substituting a solid rod for the inner tube. The rod may then be withdrawn when the operator is ready to fill the tube.

The core-rod adds considerable rigidity to the sampling tube, and since the pressure is exerted upon the solid pointed end, the tube is dragged rather than pushed into the sack, thus preventing any tendency to bend the sampling tube out of shape.

H. S. Bailey: For several years the American Oil Chemists Society has been distributing to its members and others interested samples of cottonseed and other feed meals for collaborative analysis. This work originally called the "check meal work" of the society is now known as the Smalley Foundation, in honor of the late Dr. F. N. Smalley who gave so generously of his time to make it a success.

This year 30 samples, at the rate of one each week, are being distributed to approximately 75 collaborators. These samples are analyzed for moisture, gasoline soluble material and ammonia, and the results are reported to H. C. Moore, Chief Chemist of the Armour Fertilizer Works, Chicago. Mr. Moore compiles the results and calculates what is known as the "accepted average" for percentage of oil and ammonia on each sample every week and sends a printed report to each analyst. The accepted average is not the arithmetical average but a weighted mean of all results except those obviously incorrect.

This checking up every week of the 75 or more laboratories interested in the analysis of feeds and fertilizers has, in the last four years, resulted in a marked improvement in the agreement of results. A silver cup and several certificates of accuracy are awarded every year to those making the highest standing throughout the season. This competitive feature is not the aim of the work; it is merely to add interest.

While the samples cost the members of the Oil Chemists Society $15 a year they are available to all official laboratories without charge,

the only requirement being that those accepting the samples make at least one of the determinations, oil or ammonia, each week and report their results to the chairman. Since petroleum ether instead of ethyl ether is recognized as the official solvent by the American Oil Chemists Society some of the State chemists who are already availing themselves of the samples report only moisture and ammonia. There is no required procedure for the determination of ammonia but the majority of the analysts use the mercury method.

On Sample No. 7 of this year's series which contained 6.72 per cent of ammonia, according to the accepted average, the seven State and experiment station chemists who reported varied from this average +0.03 per cent, −0.15 per cent, −0.04 per cent, +0.06 per cent, −0.02 per cent, 0.00 per cent, and −0.02 per cent. On this same sample seven laboratories of one of the large oil companies deviated from the average value by −0.01 per cent, 0.00 per cent, −0.02 per cent, −0.01 per cent, −0.00 per cent, −0.03 per cent, and +0.06 per cent.

As a concrete example of the value of these samples to the individual, the progressive increase in accuracy of a chemist in one State laboratory may be cited. On Sample No. 1 this chemist was 0.11 per cent low on ammonia; on Sample No. 2, 0.19 per cent low; on Sample No. 3, 0.36 per cent low; on Sample No. 4, 0.18 per cent low; on Sample No. 5, 0.39 per cent high; on Sample No. 6, 0.04 per cent low; on Sample No. 7, 0.15 per cent low; on Sample No. 8, 0.06 per cent low; and on Sample No. 9, 0.05 per cent high.

While the names of the chemists are not reported with their results, merely their assigned numbers being given, each collaborator is supplied with a key to these numbers and so can check himself with any other collaborator as well as with the accepted average. The results are not published in any journal nor are they intended for general information, but obviously among the collaborators the standing of any one laboratory is to some extent judged by the accuracy of its reported figures.

Either H. C. Moore or I will be very glad to see that sets of these samples are sent to any State or Federal laboratory that cares to have them and is willing to have its results printed with those of the other collaborators.

REPORT ON INORGANIC PLANT CONSTITUENTS.

By A. J. Patten (Michigan Experiment Station, E. Lansing, Mich.), *Referee.*

In carrying out the work under this subject for the past year, the plan of preceding years has been followed. The determination of sulfur and phosphorus in seeds has been handled by the associate referee, W. L. Latshaw, Manhattan, Kansas, and the work on the determination of iron and aluminium, calcium and magnesium has been conducted by the referee.

Owing to the wide difference in character between the ash of seeds and roughage materials, such as hays and straws, a tendency to adopt different methods for the two classes of materials has developed. This has resulted naturally, since methods adapted to the latter class of materials may not be adapted to the former; at least this is true as far as the present official methods for iron and aluminium, calcium and magnesium are concerned. However, if the future collaborative work on these methods bears out the conclusions drawn from the results obtained this year, one set of methods will serve for both classes of materials.

It is suggested, therefore, that the incoming referee make a study of the entire chapter on Inorganic Plant Constituents in the *Book of Methods* before another general revision is made, with a view to deleting any unnecessary methods.

REPORT ON SULFUR AND PHOSPHORUS IN THE SEEDS OF PLANTS.

By W. L. Latshaw (Agricultural Experiment Station, Manhattan' Kans.), *Associate Referee.*

The object of the work for 1922 was to secure a satisfactory method for the oxidation and preparation of solutions from plant material, including the seeds of plants, for the determination of sulfur; also to secure a method whereby the filtrate from the sulfur determination could be used for the determination of phosphorus.

Samples of cottonseed meal, soybean meal and mustardseed meal were used. Three different procedures for oxidation and solution were tried as follows:

Procedure I —*Bomb method.*
Procedure II —*Magnesium nitrate method.*
Procedure III—*Official method.*

The details of these procedures are as follows:

SULFUR.

PROCEDURE I.

The description of the apparatus, reagent, and details of oxidation and solution have been published[1].

PROCEDURE II.

REAGENT.

Magnesium nitrate solution.—Dissolve 320 grams of calcined magnesia in nitric acid, avoiding an excess of the latter; add a little calcined magnesia in excess; boil filter from the excess of magnesia, iron, etc., and dilute to 2 liters.

PREPARATION OF SOLUTION.

Weigh a 1-gram sample of the seed under examination (ground to pass a ½-mm. sieve) into a 250 cc. low-form *pyrex beaker*. Add 7.5 cc. of magnesium nitrate solution, taking care that all the material is brought in contact with the solution, and heat on an electric hot plate (at full heat 180°C.) until no further action takes place. Transfer the beaker while hot to an electric muffle and allow it to remain at low heat (muffle must not show any red) until the charge is thoroughly oxidized. No black particles should remain. (Sometimes it may be necessary to break up the charge and again return to the muffle.) Remove the beaker from the muffle and allow to cool. Add water, then hydrochloric acid in slight excess. Bring the solution to a boil and filter. The filtrate is now ready for the determination of sulfur.

The filtrate from the determination of sulfur is used for the estimation of phosphorus.

NOTE.—Reasonable care should be exercised in handling the hot pyrex beakers from the muffle and the cooler ones going into the muffle.

PROCEDURE III.

Prepare the solution according to the official method[2]. Also filter and determine sulfur as herein directed. The filtrate from the determination of sulfur may be discarded.

PHOSPHORUS.

PREPARATION OF SOLUTION.

Prepare according to the official method[3], using a 1-gram sample for the determination, as outlined under 9, (a), page 3.

DETERMINATION OF SULFUR.

Make up the solutions from the several oxidations to 200 cc., keeping the acidity to from 1–2% with hydrochloric acid (at no time having more than 2% acid). Bring the solution to a boil and add with constant stirring 10 cc. of barium chloride solution (1–9). Keep the solution on a hot plate at or near the boiling point for 5 hours (care being exercised to keep the solution as close to its original volume as possible) and then allow to stand overnight. Decant the liquid into a weighed Gooch, previously heated. Treat the precipitate with 15–20 cc. of boiling water, transfer to the filter, empty and rinse out the suction flask. Wash precipitate free from chlorides with boiling water. Dry, ignite and weigh as barium sulfate.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 469.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 20.
[3] *Ibid.*, 2

DETERMINATION OF PHOSPHORUS.

Proceed according to the official method[1]. Evaporate the filtrate from the determination of sulfur to 75 cc. if used for the determination of phosphorus.

Collaborative results on the determination of sulfur and phosphorus using three different methods, expressed as per cent.

Sulfur.

	COTTONSEED MEAL			SOYBEAN MEAL			MUSTARDSEED MEAL		
COLLABORATOR	I—BOMB METHOD	II—MAGNESIUM NITRATE METHOD	III—OFFICIAL METHOD	I—BOMB METHOD	II—MAGNESIUM NITRATE METHOD	III—OFFICIAL METHOD	I—BOMB METHOD	II—MAGNESIUM NITRATE METHOD	III—OFFICIAL METHOD
A. J. Patten,	0.49	0.54	0.50	0.37	0.43	0.41	0.87	0.89	0.85
E. Lansing,	0.50	0.54	0.45	0.34	0.42	0.40	0.89	0.89	0.83
Mich.	0.52	0.52	0.45	....	....	....	....	....	....
	....	0.52	....	....	....	....	....	....	....
Average...	0.50	0.53	0.47	0.36	0.43	0.41	0.88	0.89	0.84
O. B. Winter,	0.55	0.55	0.55	0.43	0.45	0.43	0.89	0.91	0.88
E. Lansing,	0.55	0.59	0.56	0.42	0.50	0.44	0.92	0.90	0.89
Mich.	....	0.57	....	....	0.43	....	....	....	....
	....	0.57	....	....	....	....	....	....	....
Average...	0.55	0.57	0.56	0.43	0.46	0.44	0.91	0.91	0.89
R. N. Loomis,	0.59	0.44	0.49	0.44	0.37	0.37	0.80	0.82	0.85
Manhattan,	0.56	0.46	0.50	0.38	0.36	0.36	0.81	0.82	0.85
Kans.	0.60	0.45	0.50	0.42	0.39	0.38	0.81	0.82	0.83
	0.54	0.51	0.50	0.43	0.37	0.41	0.89	0.83	0.87
	0.50	0.49	0.52	0.43	0.36	....	0.92	0.83	0.86
	0.54	0.49	....	0.45	0.35	....	0.90	0.84	....
Average...	0.55	0.47	0.50	0.43	0.37	0.38	0.86	0.83	0.85
J. F. Merrill,	0.46	0.49	0.56	0.35	0.45	0.37	0.83	0.85	0.84
Manhattan,	0.46	0.49	0.53	0.36	0.36	0.42	0.87	0.85	0.85
Kans.	0.47	0.49	0.61	0.34	0.37	0.35	0.83	0.86	0.88
	0.44	0.47	0.58	0.33	0.37	0.47	0.82	0.85	0.97
	0.48	0.49	0.57	0.35	0.37	0.46	....	0.86	0.99
	....	....	0.44	....	....	....	....	....	....
Average...	0.46	0.49	0.55	0.35	0.38	0.41	0.84	0.85	0.91
W.L.Latshaw,	0.53	0.48	0.53	0.38	0.35	0.40	0.88	0.87	0.90
Manhattan,	0.55	0.49	0.50	0.41	0.36	0.43	0.86	0.87	0.88
Kans.	0.49	0.50	0.44	0.39	0.37	0.39	0.84	0.86	0.87
	0.46	0.49	0.52	0.35	0.38	0.35	0.87	0.86	0.85
	0.51	....	....	0.34	....	....	0.85	....	....
Average...	0.51	0.49	0.50	0.37	0.37	0.39	0.86	0.87	0.88
William Ma-									
ther, College	....	0.49	....	....	0.36	....	....	0.86	....
Park, Md.	....	0.42	....	....	0.34	....	....	0.85	....
Average...	....	0.46	....	....	0.35	....	....	0.86	....

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 3, par. 9.

Phosphorus.

Collaborator	Cottonseed meal: I—Bomb method	Cottonseed meal: II—Magnesium nitrate method	Cottonseed meal: III—Official method	Soybean meal: I—Bomb method	Soybean meal: II—Magnesium nitrate method	Soybean meal: III—Official method	Mustardseed meal: I—Bomb method	Mustardseed meal: II—Magnesium nitrate method	Mustardseed meal: III—Official method
R. N. Loomis.	0.90	0.91	0.84	0.50	0.48	0.54	1.08	1.11	1.14
	0.87	0.88	0.84	0.50	0.48	0.55	1.09	1.11	1.11
	0.89	0.87	0.91	0.50	0.52	0.53	1.09	1.08	1.17
	0.89	0.91	0.91	0.53	0.55	0.55	1.14	1.13	1.15
	0.90	0.92	0.91	0.50	0.53	0.58	1.14	1.13	1.15
	0.89	0.93	....	0.52	0.55	0.55	1.16	....	1.13
Average...	0.89	0.90	0.88	0.51	0.52	0.55	1.11	1.11	1.14
J. F. Merrill.	0.82	0.85	0.94	0.44	0.45	0.53	1.06	1.07	1.18
	0.81	0.81	0.88	0.46	0.45	0.54	1.05	1.03	1.20
	0.78	0.88	1.01	0.63	0.49	0.56	1.08	1.10	1.18
	0.76	0.87	1.10	0.56	0.50	0.54	.97	1.10	1.16
	0.73	0.88	1.06	0.56	0.50	0.54	.96	1.09	1.16
Average...	0.78	0.86	1.00	0.53	0.48	0.54	1.02	1.08	1.18
W.L.Latshaw.	0.89	0.91	0.91	0.54	0.55	0.53	1.12	1.13	1.14
	0.89	0.91	0.91	0.53	0.55	0.53	1.12	1.12	1.14
	0.89	0.90	....	0.52	0.56	....	1.11	1.12	....
	0.87	0.90	....	0.52	0.55	....	1.11	1.12	....
	0.89	0.90	....	0.53	0.55	....	1.10	1.12	....
Average...	0.89	0.90	0.91	0.53	0.55	0.53	1.11	1.12	1.14

DISCUSSION.

The results of the work on the different procedures show very little difference in the percentage of sulfur found. Agreeing that the results are practically uniform the next thing to consider is ease of manipulation. It is well known to analysts who have used the present official method that it is a long and tedious procedure—one that gives the inexperienced analyst no end of trouble; it requires the use of expensive chemicals and a source of heat free from sulfur. In the case of the bomb method, the matter of sulfur-free heat is eliminated, but the expensive chemicals and apparatus must be contended with.

The magnesium nitrate method is extremely simple, requiring a small amount of inexpensive chemicals and the use of an electric hot plate and muffle furnace—appliances that are in use in practically all laboratories today. This procedure presents the further advantage in that the filtrate from the sulfur determination can be successfully used for the determination of phosphorus. The simplicity of procedure and the elimination of a large amount of sodium salts are important factors and should aid in securing more uniform results.

TOTAL SULFUR AND PHOSPHORUS.

Magnesium nitrate method.

(Applicable for plant material including seeds.)

Reagent and procedure are the same as for sulfur, page 415.
The filtrate from the barium sulfate is used for the determination of phosphorus.

RECOMMENDATIONS.

It is recommended—

(1) That the magnesium nitrate method for the determination of sulfur and phosphorus in plant materials including the seeds of plants, as outlined, be adopted as a tentative method.

(2) That the magnesium nitrate method take the place of the present official method.

REPORT ON THE DETERMINATION OF IRON AND ALUMINIUM, CALCIUM AND MAGNESIUM IN THE ASH OF SEEDS.

By A. J. Patten (Michigan Experiment Station, E. Lansing, Mich.), *Associate Referee.*

The work this year has been directed, more especially, to the determination of iron and aluminium, as the methods that have been on trial for several years for the determination of calcium and magnesium have given very satisfactory results.

In view of the fact that the ash of seeds contains a large percentage of phosphoric acid, the basic acetate method and its various modifications for the separation of iron and aluminium as phosphates were considered, but it was found that either the details of the methods had not been sufficiently worked out or they were so complicated as to be unsatisfactory.

Solutions of ferric, aluminic and calcium phosphate in hydrochloric acid were then prepared and the range of hydrogen ion concentration in which they are precipitated in the presence of ammonium acetate was determined. An amount of each solution corresponding to 0.5 gram of the phosphate was drawn off into a beaker, 25 cc. of a 25 per cent solution of ammonium acetate added, and the pH of the solution determined electrometrically. One-tenth normal ammonium hydroxide was then added in 1 cc. portions, the resulting pH being measured after each addition until the precipitation of the phosphate seemed complete. The curves obtained from plotting these results are shown in Fig. 1. The initial acidity varied with the solutions of the different phosphates.

From these curves it will be observed that the ferric phosphate alone is precipitated when the reaction of the solution shows a pH of approxi-

mately 2, and that the aluminic phosphate is precipitated at a pH of between 3 and 3.5, but that the calcium phosphate does not begin to precipitate until the pH of the solution approaches 7 and is completed at about pH 7.8. When all three phosphates were present in the same solution the ferric and aluminic phosphates seemed to be precipitated at

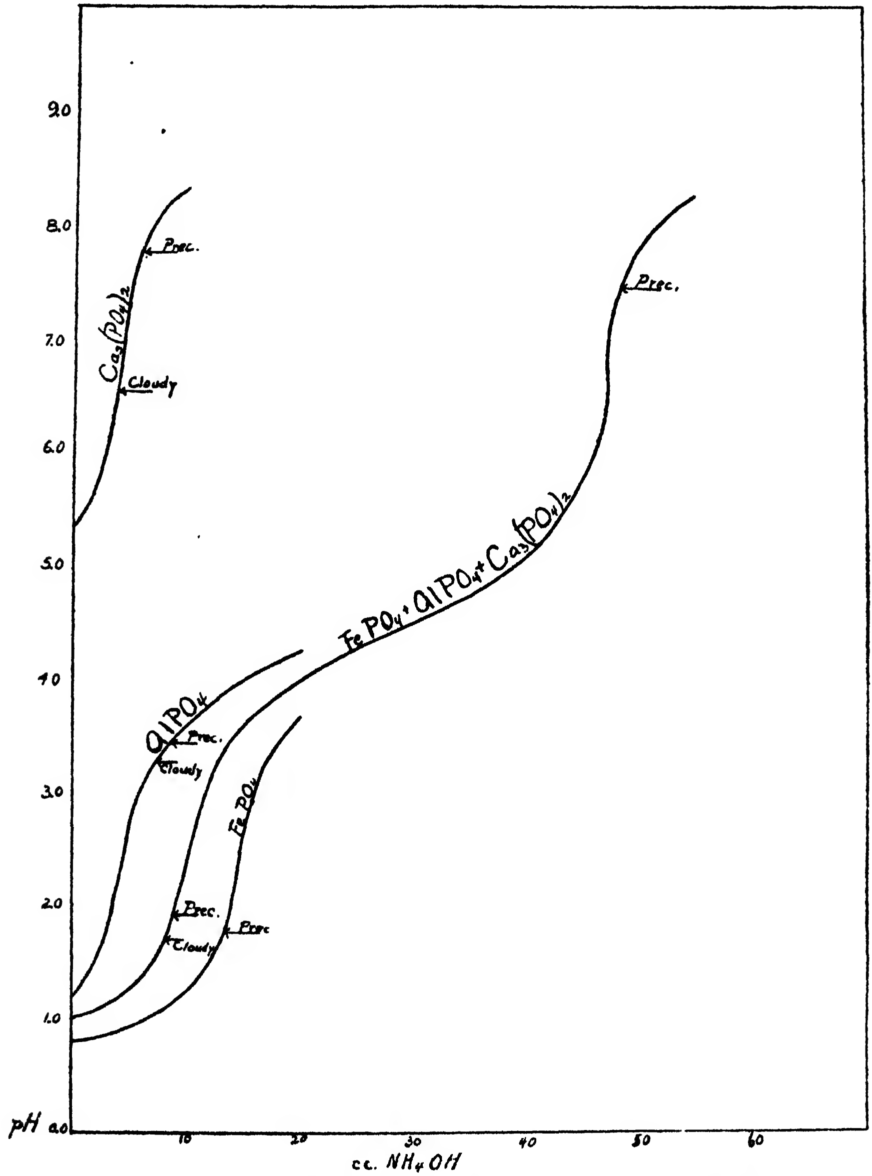


FIG. 1.—Results showing pH values at which ferric, aluminic and calcium phosphates were precipitated.

very nearly pH 2, while the calcium phosphate seemed to remain in solution until the solution showed a reading of approximately pH 7. Therefore, the range between the precipitation of ferric and aluminic phosphates and calcium phosphate in the presence of ammonium acetate seems sufficiently great to permit of their separation without much difficulty if the reaction of the solution is properly controlled.

In the actual determination of the phosphates it is sufficient to adjust the reaction of the solution to the desired pH reading, colorimetrically, using thymol blue indicator before adding the ammonium acetate. A number of trials were made using known quantities of the various phosphates to determine the reliability of the method and in nearly every case theoretical results were obtained.

It was then decided to test the methods on actual ash solutions, prepared from the following seeds: Rosen Rye, Red Rock Wheat, Wolverine Oats, Robust Beans and Two-Row Barley.

The results obtained are shown in Table 1.

TABLE 1.

Results obtained from ash solutions prepared from various seeds.

	SiO_2	$FePO_4$ + $AlPO_4$	Mn_3O_4	CaO	MgO	P_2O_5
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Rosen Rye....................	1.47	2.45	0.26	3.68	11.99	44.17
Red Rock Wheat.............	1.45	2.72	0.36	3.13	13.46	47.45
Wolverine Oats...............	28.00	2.00	0.25	4.15	8.16	31.88
Robust Beans.................	0.56	2.08	0.15	5.45	6.82	26.47
Two-Row Barley..............	1.34	1.32	0.18	2.46	13.32	40.31

After thoroughly testing the proposed methods two synthetic solutions were prepared, one to represent the ash of seeds (No. 1) and the other to represent the ash of hays and straws (No. 2).

	SOLUTION NO. 1	SOLUTION NO. 2
	Grams in 1000 cc.	*Grams in 1000 cc.*
CaO.........	0.682	3.580
MgO........	1.992	1.256
$FePO_4$.......	0.672	0.579
$AlPO_4$.......	0.543	0.457
Mn_3O_4.......	0.040	0.040
K_2O.........	5.026	5.640
Na_2O........	0.340	0.500
P_2O_5.........	7.611	1.240

A sample of each solution, in quantities of 100 cc., and a copy of the following methods of analysis were sent out to 10 laboratories:

Transfer each sample to a 200 cc. volume flask, carefully rinsing the stopper and bottle into the flask. Make to volume and take 50 cc. for analysis according to the following methods:

Iron and Aluminium.

Add four drops of thymol blue indicator and then dilute ammonium hydroxide, stirring vigorously, until the color just changes from pink to yellow. (At this point the solution should have only a faint cloudiness.) Add, while stirring, 25 cc. of a 25% solution of ammonium acetate. Heat to 70°–80°C., maintain at this temperature for about 30 minutes, allow to stand until the precipitate has settled and filter. Wash thoroughly with hot 5% ammonium nitrate solution, ignite and weigh as $FePO_4+AlPO_4$.

Manganese.

Heat to boiling the filtrate and washings from the preceding determination. Add 10–15 cc. of bromine water and continue boiling until the manganese separates as the brown oxide. If the oxidation does not take place readily add more bromine water and continue boiling until the precipitation has been completed. Place on the hot plate for 15 or 20 minutes. Filter and wash with hot water. Dry, ignite and weigh as Mn_3O_4.

Calcium.

Concentrate the filtrate and washings from the preceding determination to 150–200 cc. Add 10 cc. of 0.5N hydrochloric acid and 10 cc. of 2.5% oxalic acid. Boil the solution, add with constant stirring 15 cc. of a saturated solution of ammonium oxalate, and continue to heat until the precipitate becomes granular. Allow to stand 4–12 hours. Filter, wash with hot water until free from chlorides, ignite, heat over a blast lamp and weigh as CaO. If preferred the precipitate of calcium oxalate, after washing, may be dissolved in hot dilute sulfuric acid (1–5) and titrated with 0.1N potassium permanganate solution.

Magnesium.

To the combined filtrate and washings from the calcium determination, add 15 cc. of strong nitric acid and evaporate to dryness. Take up with dilute hydrochloric acid and make to a volume of about 100 cc. Add 1–2 grams of di-sodium hydrogen phosphate, or enough to precipitate all the magnesium. When cold, make slightly alkaline with ammonium hydroxide, stirring constantly. Add 5–10 cc. of ammonium hydroxide

TABLE 2.

Collaborative results obtained from synthetic solutions representing the ash from seeds (Solution No. 1) and from straws and hays (Solution No. 2).

ANALYST	$FePO_4+AlPO_4$		Mn_3O_4		CaO		MgO	
	Solution No. 1	Solution No. 2	Solution No. 1	Solution No. 2	Solution No. 1	Solution No. 2	Solution No. 1	Solution No. 2
1	39.6*	32.4*	0.9	1.7	15.0	87.5	49.8	30.8
2	32.0	25.9	2.1	2.1	19.1	90.8	49.7	30.7
3	36.2*	30.3*	2.2	3.0	23.7*	97.9*	56.1*	42.6*
4	30.7	26.0	1.1	0.6	17.2	91.1	50.4	32.1
5	32.3	26.1	1.7	1.4	16.1	91.8	50.8	32.1
6	32.3	25.9	2.2	2.1	17.9	90.3	50.6	33.2
7	32.1	26.9	2.5	2.5	18.5	90.7	50.5	31.8
8	31.0	25.5	1.0	1.9	17.1	90.3	49.3	31.5
Average.....	31.7	26.1	2.0	1.8	17.3	90.4	50.2	32.0
Theory......	30.5	25.8	1.0	1.0	17.1	89.5	49.8	31.4

* Omitted from average.

in excess and allow to stand about 12 hours. Filter, wash with a solution of 2.5 per cent ammonium hydroxide until free from chlorides, ignite, heat over a blast lamp and weigh as magnesium pyrophosphate. Calculate to MgO.

Reports were received from 8 laboratories. The results, expressed in milligrams per 25 cc. of the original solution, are given in Table 2.

DISCUSSION.

The results are unusually good with the exception of those for iron and aluminium by Analyst No. 1 and those by Analyst No. 3.

High results for iron and aluminium may be obtained if the neutralization of the solutions with ammonium hydroxide is carried too far; in which case some calcium may be carried down. In the case of Analyst No. 1 it seems probable that this is what happened as in both samples the results for calcium are below the theoretical amounts. Concerning the results by Analyst No. 3 it is difficult to understand why those for calcium and magnesium should also be high unless the precipitates were not ignited to constant weight.

The results obtained for manganese varied greatly but it was not expected that this method would be reliable for such small quantities. The colorimetric method for manganese[1] which has already been adopted as official should be used where an accurate determination is desired. No attempt was made to determine the iron and aluminium separately as the well-known method of fusing with potassium hydrogen sulfate has already been thoroughly tested and adopted as official[2].

RECOMMENDATION.

It is recommended—

That the methods for iron, aluminium, calcium and magnesium as given in this report be further studied with a view to their adoption as tentative methods.

REPORT ON DAIRY PRODUCTS.

By JULIUS HORTVET (State Dairy and Food Commission, St. Paul, Minn.), *Referee*.

No collaborative work has been conducted by the referee during the past year. The results of investigations made during 1919, 1920 and 1921 are deemed sufficiently conclusive to place the cryoscopic method of examination of milk on a substantial basis. A large number of authentic samples of milk obtained from individual cows and herds have already been subjected to careful tests, and the natural range of freezing-

[1] *J. Assoc. Official Agr. Chemists*, 1921, 4: 393.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 16, par. 6; 29, par. 43.

point depressions has been reasonably substantiated by the experience of a number of collaborators. The actual limits of reliability of freezing-point results have been amply illustrated in the reports presented by the referee during the past two years. Valuable assistance has been rendered by the associate referee in the investigation of samples obtained under abnormal conditions as well as normal samples taken from individual cows and herds. The results of further work conducted along lines suggested in connection with the report of a year ago will be presented by the associate referee. For the purpose of presenting the cryoscopic method in final form for action on the part of the association the text has been carefully revised and rewritten, care being taken that no essential details of the method, as presented in the report of a year ago, were altered. The description of the method is grouped under headings as follows:

1. *Apparatus:*
   (a) The Cryoscope.
   (b) The Thermometer.

2. *Standardization of the Thermometer:*
   A method of testing the thermometer scale followed by an explanation of the use of a correction factor to be applied to the observed freezing-point depression.

3. *Cryoscopic Procedure:*
   The following text is descriptive of the procedure for the collection of milk samples for chemical analysis and of the cryoscopic method for the examination of milk and is submitted as a final report on this subject:

COLLECTION OF SAMPLES FOR CHEMICAL ANALYSIS.

Each sample shall consist of at least one quart.

Bottled milk may be sampled by the collection of one or more bottles as prepared for sale.

Bulk milk must be thoroughly mixed before the sample is withdrawn. This is best accomplished by pouring the milk from one vessel into another three or four times. Where this is impossible, the milk should be thoroughly and vigorously stirred for at least half a minute with a suitable appliance long enough to reach to the bottom of the container. If cream has formed on the milk, the mixing must be continued until all cream is detached from the sides of the vessel and evenly emulsified throughout the liquid. The sample should be withdrawn into clean, dry, air-tight glass jars and if transported by mail, express or otherwise, the sample bottles should be completely filled, tightly stoppered and properly sealed

and marked for identification. The samples should be kept in a cool place (2°–5°C.) but not allowed to freeze until ready for examination.

Immediately before withdrawing portions for the analytical determinations, the sample should invariably be poured into a clean empty vessel and back in order to insure a homogeneous mixture.

THE CRYOSCOPIC EXAMINATION OF MILK.

1 APPARATUS.

(a) *The Cryoscope.*—A description of the cryoscope has been published[1]. The apparatus should be set up as carefully and correctly as possible. All connections should be sufficiently tight to avoid escape of ether vapors. Care should be taken to avoid breakage of the Dewar flask. The perforated loop at the lower end of the metal inlet tube should be adjusted to a position about 3 cm. above the bottom of the flask. The rubber tube connecting the air-drying tube with the air-inlet tube should be extended so as to cover the metal tube as far as the top surface of the cork. When removing the upper section of the cryoscope withdraw the glass tube which is inserted in the cork stopper at the top of the air-drying device.

The bulb of the control thermometer should extend to a position about three-fourths of the distance from the surface of the 400 cc. ether level to the bottom. When the thermometer has been properly inserted in the cork it should remain in position unless for a special reason it may be necessary to withdraw it.

Prepare a glass ether-level gage of suitable length for inserting to within a short distance above the bottom of the flask. Insert over the upper end of the gage tube a short section of rubber tubing for the purpose of preventing breakage of the vacuum flask when the tube is inserted into the ether. The lower end of the tube should be provided with file marks indicating various ether levels, viz., 200 cc., 300 cc., 400 cc., etc.

Place a plug of cotton in the funnel tube (preferably a narrow short-stemmed thistle tube) for the purpose of separating impurities which may be present in the ether when being poured into the cryoscope.

Pour into the air-drying tube only sufficient concentrated sulfuric acid to just cover the perforations in the small bulb near the bottom of the tube. Do not allow the sulfuric acid to rise to a level near the perforations at the shoulder of the mantle.

The stirrer and freezing starter should both move freely in the metal tubes provided for them in the rubber stopper which holds the standard thermometer.

[1] *J. Ind. Eng. Chem* 1921, 13: 198; *J. Assoc. Official Agr. Chemists*, 1921, 5: 173.

Keep the freezing starter in contact with a small block of ice for some minutes before applying it, as directed in the procedure **3**.

Adjust the pump and regulate the pressure in such a manner that air will be forced through the apparatus at a fairly rapid rate, avoiding splashing or excessive foaming of the sulfuric acid. When all adjustments are properly made and a free passage of air is maintained through the apparatus it is possible to lower the temperature of the ether bath from approximately +20°C. to 0°C. in from 5 to 10 minutes. When the cooling action appears to be retarded the sulfuric acid must be removed from the drying tube and a fresh supply poured in.

The ether drain tube on the left side of the cryoscope should carry off the vapor into the sink. No marked odor of ether should be noticeable at the top portion of the tube. When the cryoscope is not in use place a plug of cotton in the top of the drain tube in order to check loss of ether by evaporation. Remove the cotton when the apparatus is in use.

The glass tube at the back portion of the cryoscope stand is intended for holding the thermometer when it is removed from the freezing test-tube. Place a pad of cork or rubber at the bottom of the tube to serve as a rest for the thermometer bulb.

(b) *The Thermometer.*—Examine the thermometer very carefully, using a lens if necessary, in order to determine whether any defects exist in the glass or in the mercury thread. Dislodge any particle of mercury which may be adhering to the inner surface of the expansion space at the top of the stem. Also dislodge any gas bubble which may be noticeable in the bulb or which may form a separation at any part of the mercury thread. When the thermometer is brought into proper condition for use make standardization tests according to directions given under **2**.

Keep the thermometer always in an upright position. In removing from the stopper or reinserting do not turn the thermometer to an inverted position and avoid a horizontal position as much as possible. When the thermometer has been properly adjusted and carefully tested it should be handled at all times with great care.

Test the thermometer at frequent intervals, once a week or as often as may be necessary, in order to keep an accurate record of any changes which may occur. Determine the true 0-position and the depression produced by a standard sucrose solution often enough to be certain at all times regarding the reliability of results.

(c) *The Control Thermometer.*—Test the control thermometer in a bath of melting crushed ice for the purpose of determining whether the 0-mark on the scale is correct. The scale graduations should be accurate to within 0.1°C.

2 STANDARDIZATION OF THE THERMOMETER.

Make freezing-point determinations on the following:

(a) *Recently boiled distilled water.*

(b) *7 grams sucrose solution.*—Dissolve 7 grams of pure sucrose in pure water and make the solution up to a volume of exactly 100 cc. at 20°C.

(c) *10 grams sucrose solution.*—Dissolve 10 grams of pure sucrose in pure water and make the solution up to a volume of exactly 100 cc. at 20°C.

A sample of pure sucrose may be obtained by application to the Director of the Bureau of Standards, Department of Commerce, Washington, D. C.

Make three freezing-point determinations on the distilled water and on each of the sucrose solutions according to the procedure described in **3** and tabulate the results in the following form:

FREEZING-POINT OBSERVATIONS	PURE WATER	7 GRAMS SUCROSE SOLUTION		10 GRAMS SUCROSE SOLUTION	
		Observed Freezing Point (-S)	Freezing-Point Depression S-W (Algebraic)	Observed Freezing Point (-S)	Freezing-Point Depression S-W (Algebraic)
1st					
2nd					
3rd					
Averages	±W	xxxxxx		xxxxxxx	

Express the results as degrees freezing-point *depression* below the *average* of the observed freezing points obtained on the sample of pure water (±W), which may be above (+) or below (−) the 0-mark on the scale. Obtain each freezing-point depression of the sucrose solutions by the *algebraic subtraction* of the *average* of the freezing-point readings of pure water (±W) from each observed freezing point.

Omit adventitious results, *i. e.*, results which are in marked disagreement with other results obtained by carefully following instructions.

Apply the average of the freezing-point depressions obtained on the standard sucrose solutions for the purpose of correcting the thermometer readings obtained on samples of milk in the manner illustrated in the report of the referee for 1921[1].

3 CRYOSCOPIC PROCEDURE.

Insert the funnel-tube into the vertical portion of the T-tube at one side of the apparatus and pour in 400 cc. of ether previously cooled to

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 477.

10°C. or lower. Close the vertical tube by means of the small cork and connect the pressure pump to the inlet tube of the air-drying attachment. Adjust the pump so as to pass air through the apparatus at a moderate rate, as may be judged by the agitation of the sulfuric acid in the drying tube. Continuous vaporization of the ether will cause a lowering of the temperature in the flask from ordinary room temperature to 0°C. in from 5 to 10 minutes. Continue the temperature lowering until the control thermometer registers near −3°C. At this stage, by lowering the gage tube into the ether bath, then closing the top by means of the forefinger and raising to a suitable height, an estimate can be made as to the amount of ether necessary to pour in for the purpose of restoring the 400 cc. volume. When the volume of ether has been adjusted to 400 cc. an additional 10 to 15 cc. is sufficient on an average for each succeeding determination. Pour into the freezing test-tube 30 to 35 cc. of boiled distilled water, cooled to 10°C. or lower, or enough to fairly submerge the thermometer bulb. Insert the thermometer together with the stirrer and lower the test-tube into the larger tube. A small quantity of alcohol, sufficient to fill the lower space between the two test-tubes, will serve to complete the conducting medium between the freezing bath and the liquid to be tested. Keep the stirrer in steady up-and-down motion at a rate of approximately one stroke each two or three seconds, or even at a slower rate, providing the cooling proceeds satisfactorily. Maintain passage of air through the apparatus until the temperature of the cooling-bath reaches −2.5°C., at which time the top of the mercury thread in the thermometer usually recedes to a position in the neighborhood of the freezing point of water. Maintain the temperature of the cooling-bath at −2.5° and continue the manipulation of the stirrer, until a super-cooling of sample 1.0° to 1.2° is observed. As a rule, at this time the liquid will begin to freeze, as will be noted by the rapid rise of the mercury. Manipulate the stirrer slowly and carefully three or four times as the mercury column approaches its highest point. By means of a suitable light-weight cork mallet tap the upper end of the thermometer cautiously a number of times until the top of the mercury remains stationary a couple of minutes. Taking necessary precautions to avoid parallax, observe the exact reading on the thermometer scale and estimate to 0.001°C. When the observation has been satisfactorily completed make a duplicate determination, then remove the thermometer and stirrer and empty the water from the freezing tube. Rinse out the tube with about 25 cc. of the sample of milk, cooled to 10°C. or lower, measure into the tube 30 to 35 cc. of the milk, or enough to fairly submerge the thermometer bulb, and insert the tube into the apparatus. Maintain the temperature of the cooling-bath at 2.5° below the probable freezing point of the sample. Make the determination on the milk following the same procedure as that

employed in determining the freezing point of water. As a rule, however, it is necessary to start the freezing action in the sample of milk by inserting the freezing starter, in the open end of which has been wedged a fragment of ice, at the time when the mercury column has receded to 1.0°–1.2° below the probable freezing point. A rapid rise of the mercury results almost immediately. Manipulate the stirrer slowly and carefully two or three times while the mercury approaches its highest point. Complete the adjustment of the mercury column in the same manner as in the preceding determination; then, avoiding parallax, observe the exact reading on the thermometer scale and estimate to 0.001°. The *algebraic difference* between the average of the readings obtained on the water and the reading obtained on the sample of milk represents the *freezing-point depression* of the milk. Apply necessary correction to the result in the manner illustrated under **2.**

To deduce the percentage of added water from the determined freezing-point depression, use Winter's table[1] or the scale accompanying the cryoscope. The percentage of added water (W) may also be calculated as follows:

$$W = \frac{100\,(T-T')}{T}\text{, in which}$$

T = the average freezing point of normal milk (−0.550°C.); and
T′ = the observed freezing point on a given sample.

Make freezing-point determinations only on samples of milk which are fairly sweet or fresh, *i. e.*, samples which show an acidity test of not appreciably more than 0.01 per cent above 0.15 per cent (expressed in terms of lactic acid). Make the acidity determination according to the following method:

Measure out 17.6 cc. of the milk, using a 17.6 cc. Babcock pipet, dilute with an equal volume of water (free from carbon dioxide), washing out the pipet with the same, add 0.5 cc. of phenolphthalein indicator, and titrate with 0.1N sodium hydroxide. The number of cc. of 0.1N sodium hydroxide required to neutralize the sample of milk divided by 20 gives the percentage of lactic acid.

A minimum freezing-point depression of −0.530°C. and a maximum of −0.566°C. for milk from normal individual cows and a minimum of −0.530°C. and a maximum of −0.562°C. for milk from normal herds is substantiated by collaborative work carried out in various parts of the country on approximately 300 samples. Owing to these observed natural variations it is advisable to adopt a tolerance figure in passing judgment on market samples. A tolerance of 3 per cent may be deducted from results for added water calculated on the basis of an average freezing-point depression of −0.550°. A thorough investigation of the

[1] *Chem. News*, 1914, **110**: 283.

cryoscopic properties of authentic samples in a given locality may justify a smaller, but scarcely a larger, tolerance figure. Owing to the narrow variations actually found among market milks of genuine character, it is not necessary in practice to deduct the tolerance figure from results showing added water in amounts above 3 per cent.

RECOMMENDATION.

It is hereby recommended—

That the cryoscopic method for the examination of milk be adopted as an official method of this association.

No report on moisture in cheese was made by the referee. See page 437.

CRYOSCOPY OF MILK.

By E. M. Bailey (Agricultural Experiment Station, New Haven, Conn.), *Associate Referee.*

In the report of the associate referee for 1921 the three following topics were suggested for further study: the correction of freezing point to be made for increased acidity; the effect of pathological conditions of the animals upon the freezing-point depression of milk; and corroboration, if possible, of certain abnormal freezing points reported at that time.

The work this year has been confined to consideration of these subjects.

INFLUENCE OF ACIDITY UPON FREEZING-POINT DEPRESSION OF MILK.

The cause of the acidity which fresh milk shows toward phenolphthalein has been the subject of much investigation. Carbon dioxide, acid salts and casein, separately or in various combinations, generally have been regarded as responsible for the so-called apparent acidity of normal milk in a fresh condition. To accept the careful studies of Van Slyke and his co-workers, however, the acidity of fresh milk is due to the presence of acid phosphates[1]; the acidity decreases with increasing carbon dioxide content[2]; and casein is combined with calcium as a calcium caseinate which is neutral to phenolphthalein. As milk ages another type of acidity appears, due chiefly to bacterial decomposition of lactose with the formation of lactic acid. Examination of samples of milk, under induced souring, taken at intervals up to 96 hours showed that the figures representing increases of the acidity in the milk were almost identical with those representing the determined amounts of lactic acid[3]. In these experiments the degree of acidity was determined by titration

---

[1] Van Slyke and Bosworth, New York Agr. Exp. Sta. Tech. Bull. 37, 1914.
[2] Van Slyke and Baker, *J. Biol. Chem.*, 1919, 40, 345.
[3] Van Slyke and Bosworth, New York Agr. Exp. Sta., Tech. Bull. 48, 1916.

with 0.1N alkali, using phenolphthalein as an indicator, but first removing calcium by means of neutral potassium oxalate to avoid the error otherwise introduced by the hydrolysis of dicalcium phosphate during titration. The results obtained in this way are about one-half as great as those obtained by the usual method of titration.

In applying the freezing-point test as a means of detecting added water in milk the question of the influence of acidity has been raised. Without other complicating factors it would be expected that the mere increase in amount of lactic acid would result in a corresponding increase in freezing-point depression. Keister[1] has studied this point, and additional data have been obtained by the associate referee during the past year. The combined data are given in Table 1. Acidity is the result of spontaneous souring in these trials, and it has been determined and expressed according to the uniform plan followed in work reported last year[2].

A study of the results in Table 1 shows that the effect of increased acidity upon freezing-point depression is an additive factor, and that the magnitude of the increased depression closely approximates 0.003°C. for each 0.01 per cent increase in acidity. If we may broadly assume acidities less than 0.25 per cent due to normal variations in fresh milk and figures in excess of that amount due to lactic acid, then with this distinction in mind, closer examination of the results shows that there is greater uniformity in depression increments per unit of acidity in the lactic acid stage than obtains in the stage of apparent acidity. The data on acidity intervals within the range of apparent or normal acidity are chiefly furnished by the figures quoted from Keister's tabulation; but in any case it is recognized that measurements within this restricted range, especially when acidity determinations are made by means of titration, are necessarily attended with greater opportunities for experimental error. The practical deduction to be drawn from these data is that a correction for acidity ought to be made in the observed freezing-point depression when it is required to examine milk which is sensibly sour. The numerical definition of this point in terms of acidity will obviously vary in different samples. Steuart[3] observed that the acidity of fresh milk from individual cows varied from 0.10 to 0.21 per cent, and that of commercial mixed milk varied from 0.16 to 0.20 per cent. McNerney[4] noted practically the same limits, and they are further substantiated by the figures contained in the report of the associate referee last year[5]. Sommer and Hart[6], however, cite an instance of fresh herd milk with an acidity of 0.257 per cent which was not sour as judged by the evidence

[1] *J. Ind. Eng. Chem.*, 1917, 9: 862.
[2] *J. Assoc. Official Agr. Chemists*, 1922, 5: 471.
[3] *J. Dairy Sci.*, 1920, 3: 52.
[4] *Ibid.*, 227.
[5] *J. Assoc. Official Agr. Chemists*, 1922, 5: 484.
[6] *J. Dairy Sci.*, 1921, 4: 7.

of smell or taste. In general, it would appear that acidities in excess of 0.20 or 0.25 per cent result from fermentation and will represent milk which is sour or near the "turning" point. No correction of freezing point is recommended for acidity within the normal range for fresh milk—that is to say, milk showing an acidity not exceeding 0.25 per cent.

FREEZING POINT OF MILK FROM TUBERCULAR COWS.

Milk from individual cows in a herd consisting of six Jerseys was examined. The first series of samples was taken three days after all

TABLE 1.

Influence of acidity upon the freezing-point depression of milk.

NO.	DESCRIPTION OF SAMPLE	DATE 1922	ACIDITY	FREEZING POINT	INCREASE IN ACIDITY	INCREASE IN F.-P. DEPRESSION	INCREASE IN F.-P. DEPRESSION PER 0.01 % INCREASE IN ACIDITY
			per cent	−0°C.	*per cent*	°C.	°C.
18169	Pasteurized	11-16	0.130	0.530	.....	. . .	.....
		11-17	0.130	0.530	.. .	.....	....
		11-18	0.460	0.627	0.330	0.097	0.0029
	Average (based on total increases)......				0.330	0.097	0.0029
21667	Market......	2-3	0.215	0.560	.....	.....	.....
		2-4	0.335	0.600	0.120	0.040	0.0033
		2-5	0.405	0.623	0.070	0.023	0.0033
		2-6	0.510	0.653	0.105	0.030	0.0029
		2-7	0.580	0.672	0.070	0.019	0.0027
	Average....	.....	....	....	0.365	0.112	0.0031
21668	Market......	2-3	0.205	0.550	. ...	.....	.....
		2-4	0.300	0.584	0.095	0.034	0.0036
		2-5	0.400	0.620	0.100	0.036	0.0036
		2-6	0.535	0.656	0.135	0.036	0.0027
		2-7	0.600	0.673	0.065	0.017	0.0026
	Average....	.....	....	....	0.395	0.123	0.0031
18706	Raw.........	2-6	0.140	0.539	.....	.....	.....
		2-7	0.140	0.539	.....	.....	. ...
18707	Raw.........	2-7	0.150	0.540	.....	.....	.....
		2-11	0.250	0.570	0.100	0.030	0.0030
		2-14	0.550	0.660	0.300	0.090	0.0030
	Average....	.....	....	....	0.400	0.120	0.0030
18708	Raw.........	2-8	0.150	0.541	.....	.....	.....
		2-11	0.220	0.567	0.070	0.026	0.0037
18733	Raw.........	2-15	0.145	0.530	.....	.....	.....
		2-16	0.150	0.530	0.005	0.000	.....
		2-17	0.225	0.555	0.075	0.025	0.0033
		2-18	0.415	0.613	0.190	0.058	0.0031
	Average....	. ....	....	....	0.270	0.083	0.0031
18734	Raw.........	2-16	0.150	0.541	.....	.....	.....
		2-18	0.310	0.590	0.160	0.049	0.0031

TABLE 1—*Continued.*

Influence of acidity upon the freezing-point depression of milk.

(From Keister's Table III)*

NO.	DESCRIPTION OF SAMPLE	DATE 1922	ACIDITY	FREEZING POINT	INCREASE IN ACIDITY	INCREASE IN F.-P. DEPRESSION	INCREASE IN F.-P. DEPRESSION PER 0.01 % INCREASE IN ACIDITY
			per cent	*–°C.*	*per cent*	*°C.*	*°C.*
1	Pasteurized...	......	0.15	0.545	.....	.....	.....
		......	0.18	0.548	0.03	0.003	0.0010
		......	0.42	0.637	0.24	0.089	0.0037
	Average....	......	....	....	0.27	0.092	0.0034
2	Pasteurized...	......	0.15	0.509	.....	.....	.....
		......	0.18	0.548	0.03	0.009	0.0030
		......	0.34	0.602	0.16	0.054	0.0034
	Average....	......	....	....	0.19	0.063	0.0033
3	Pasteurized...	......	0.18	0.496	.....	.....	.....
		......	0.21	0.515	0.03	0.019	0.0063
		......	0.24	0.522	0.03	0.007	0.0023
		......	0.27	0.536	0.03	0.014	0.0047
	Average....	......	....	....	0.09	0.040	0.0044
4	Pasteurized...	......	0.15	0.552	.....	.....	.....
		......	0.17	0.555	0.02	0.003	0.0015
		......	0.20	0.558	0.03	0.003	0.0010
		......	0.46	0.636	0.26	0.078	0.0030
	Average....	......	....	....	0.31	0.084	0.0027
5	Pasteurized...	......	0.16	0.541	.....	.....	.....
		......	0.18	0.546	0.02	0.005	0.0025
		......	0.22	0.564	0.04	0.018	0.0045
	Average....	......	....	....	0.06	0.023	0.0038

**J. Ind. Eng. Chem.*, 1917, 9: 864.

the animals had been subjected to the tuberculin test. The second series was taken about one week after the first.

The data presented last year showed that freezing points of milk from tubercular reactors or cows otherwise abnormal physically were generally within the limits for normal milk. The few exceptions noted were in the direction of decreased depressions.

In the case of the herd examined this year no figures outside the limits suggested a year ago for normal milk were obtained.

It is further noted in the work of Van Slyke and Baker[1] that a number of instances of garget did not cause the milk to show abnormal freezing-point depression.

[1] New York Agr. Expt. Sta. Tech. Bull. 71, 1919.

TABLE 2.

Freezing point of milk from tubercular cows.

HERD	COW NO.	DATE 1922	SPECIFIC GRAVITY	SOLIDS	FAT	SOLIDS NOT FAT	ACIDITY	FREEZING POINT
				per cent	*per cent*	*per cent*	*per cent*	*-0°C*
M.	1	3-21 A. M.	1.0325	13.54	4.5	9.04	0.14	0.544
	Non-	P. M.	1.0323	13.49	4.5	8.99	0.13	0.549
	reactor	3-27 A. M.	1.0309	13.02	4.4	8.62	0.13	0.539
		P. M.	1.0317	13.12	4.3	8.82	0.12	0.546
	2	3-21 A. M.	1.0333	13.62	4.4	9.22	0.14	0.543
	Reactor	P. M.	1.0323	13.37	4.4	8.97	0.14	0.539
		3-27 A. M.	1.0323	13.22	4.3	8.92	0.13	0.546
		P. M.	1.0326	13.57	4.5	9.07	0.13	0.539
	3	3-21 A. M.	1.0338	13.63	4.3	9.33	0.15	0.550
	Reactor	P. M.	1.0333	14.10	4.8	9.30	0.14	0.549
		3-27 A. M.	1.0327	13.47	4.4	9.07	0.13	0.544
		P. M.	1.0327	13.47	4.4	9.07	0.13	0.540
	4	3-21 A. M.	1.0343	15.08	5.4	9.68	0.14	0.550
	Reactor	P. M.	1.0345	15.00	5.3	9.70	0.15	0.549
		3-27 A. M.	1.0323	14.08	5.0	9.08	0.13	0.540
		P. M.	1.0336	14.66	5.2	9.46	0.14	0.544
	5	3-21 A. M.	1.0333	14.46	5.1	9.36	0.17	0.548
	Non-	P. M.	1.0335	15.00	5.5	9.50	0.16	0.549
	reactor	3-27 A. M.	1.0330	14.76	5.4	9.36	0.17	0.559
		P. M.	1.0331	15.02	5.6	9.42	0.17	0.545
	6	3-21 A. M.	1.0335	14.27	4.9	9.37	0.17	0.562
	Reactor	P. M.	1.0326	14.05	4.9	9.15	0.16	0.553
		3-27 A. M.	1.0318	14.09	5.1	8.99	0.16	0.554
		P. M.	1.0332	13.84	4.6	9.24	0.16	0.549

ABNORMAL SAMPLES.

In the report of 1921 eleven freezing points which were distinctly outside the tentative limits suggested were noted with the reservation that they required further corroboration. Ten of these results that exceeded the maximum depression limit of −0.566°C. ranged from −0.570° to −0.580°C.; one was outside the minimum limit of −0.530°C. All these results were obtained on milk from individual cows of one herd, and this herd was studied further this year. Forty samples from nineteen individual cows of the herd and two samples of the mixed milk of the herd were examined, with the result that only one freezing point outside the tentative limits was observed, and that exceeded the maximum by a negligible amount, *viz.*, 0.002°. The summaries for acidity and freezing-point depression are as follows:

In connection with this particular phase of the subject, H. C. Lythgoe cited a number of instances of abnormal milks which came to his attention during the past year. Since these milks were abnormal in other respects than freezing-point depression they do not essentially

affect the writer's conclusions with reference to the freezing-point range of milk from normal individual cows in the sense of the term "normal", as contemplated and reported last year.

TABLE 3.

Summaries for acidity and freezing-point depression.

	ACIDITY	FREEZING POINT
Individual cows:	*per cent*	-0°C.
Maximum....	0.15	0.568
Minimum....	0.10	0.532
Average....	0.13	0.547
Herd:		
Average ...	0.14	0.554

By way of general comment on the cryoscopic method, Mr. Lythgoe expressed the opinion that the serum refraction and sour serum ash considered together are as efficient as the freezing point as a means of detecting added water, but he agreed that the freezing-point depression is a factor which is less variable than any other single determination ordinarily made in the examination of milk.

CONCLUSION.

The value of the cryoscopic method as an adjunct to present methods for detecting added water in milk is fully demonstrated by data covering a period of more than two years. Its use may be optional when present methods furnish conclusive evidence; but, in the experience of the majority of collaborators, its unique value is shown in those cases where the evidence of present methods is conflicting or inconclusive. The tentative limits for normal milk may have to be modified; but since the value of this, or any similar method, is lessened as the limits of normal variation are widened, it is believed that the limiting values as defined in the report of last year should remain until there is further evidence that they should be modified. It should be emphasized that in all exceptional cases recourse may be had to the examination of authentic milk from the particular source in question, and the decision made on the basis of the evidence so obtained.

Collaborators who contributed to the work this year are R. E. Andrew, Connecticut Experiment Station, New Haven, and S. H. Hall, State Board of Health, Boston. H. C. Lythgoe, chief of the Boston laboratory, submitted data and criticism.

METHODS FOR FAT IN MALTED MILK AND DRIED MILK.

By J. T. KEISTER (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*

The work during the past year has been a continuation of the work along the same line reported at the 1921 meeting[1], *viz.*, a comparative study of the "neutral" procedure in which the ammonia is omitted in the regular Roese-Gottlieb method with one modification. This modification consists in preparing a 15 or 20 per cent water solution of the sample for the fat determination, instead of weighing out about one gram of the powder.

The proposed method is described as follows:

PREPARATION OF SAMPLE.

Weigh out 15 grams of the well-mixed sample and 85 grams of distilled water; warm the water slightly and mix the water and malted milk with a glass rod to assist in getting all lumps in solution. Cool the solution to room temperature, agitate and weigh out accurately about 10 grams into a small cylinder; then transfer to a Röhrig tube or similar apparatus.

DETERMINATION.

Add 10 cc. of 95% alcohol, shake thoroughly and proceed as in the official Roese-Gottlieb method[2] for milk, condensed milk and ice cream, washing out the cylinder with portions of the ether. Make two extractions using 25 cc. of each ether, then a third extraction using 15 cc. of each ether, transferring the third extract to a separate flask. The third extraction usually yields less than 1 mg. of fat. Small amounts of non-fatty material are sometimes dissolved in the extraction process (almost always in the case of malted milk substitutes), correction for which should be made by dissolving out the fat with petroleum ether, drying the insoluble residue and weighing.

In connection with the majority of the samples which were not true malted milk, some difficulty was encountered in carrying out the neutral process, in that a more or less heavy precipitation or coagulation took place on adding the alcohol, which condition probably accounts in some measure for the non-fatty residue accompanying the fat in some samples. This condition was particularly noticeable in the case of Samples Nos. 4, 10 and 12. There was also a tendency toward a settling out or partial separation of the solids in the case of solutions of malted milk substitutes, which difficulty necessitated extra precaution in weighing out samples. These difficulties were, however, not experienced with samples of genuine malted milk. It will also be noted that practically all the malted milk substitutes yield a very small percentage of fat, and no appreciable differences are noted between results obtained by the neutral and alkaline methods of extraction.

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 507.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 227.

In the case of true malted milks, a 15 per cent solution was found to give very satisfactory results, but in the case of samples of lower fat content a 20 per cent solution was used with apparent advantage. In trials made with solutions of true malted milk, the amount of fat obtained by a third extraction indicated that a 15 per cent solution was preferable.

The results appear to be very satisfactory and the neutral process in the majority of cases yields a higher percentage of fat than the regular Roese-Gottlieb procedure. In this connection it should be stated that in the few cases where the above statement does not hold the product was a compound and not a true malted milk.

Results of fat determinations in malted milk.

(Calculated to a water-free basis.)

SAMPLE NO.	FAT BY NEUTRAL PROCEDURE	FAT BY ROESE-GOTTLIEB METHOD	REMARKS
	per cent	*per cent*	
1C	9.64	9.48	15% solution used.
	9.67	9.366	
1D	9.44	9.27	15% solution used.
	9.52	9.36	
1E	8.87	8.74	20% solution used.
	8.96	8.85	
1A	8.547	8.38	20% solution used.
	8.558	8.44	
2	8.36	8.14	....
	8.305	8.23	
3	11.967	11.86	15% solution used. Product labeled "A compound of malt and milk".
	11.946	11.905	
4	1.207	1.069	15% solution used. Product labeled "A compound of malt and milk".
	1.14	1.08	
5	1.45	1.395	20% solution used. Product said to contain malt, skim milk powder, sugar and salt.
	1.45	1.405	
6	1.58	1.429	20% solution used. Product labeled "Malted skimmed milk".
	....	1.437	
7	11.58	11.57	20% solution used.
	11.588	11.575	
8	9.157	9.117	15% solution used.
	9.22	9.01	
9	6.82	6.79	15% solution used.
	6.775	6.84	
10	0.646	0.619	20% solution used. Product labeled "A compound of malt, skim milk and cereals".
	0.69	0.64	
11	0.59	0.533	20% solution used. Product labeled "A compound of malt, skim milk and sugar".
	0.609	0.572	
12	1.799	1.726	20% solution used. Product labeled "Skim milk and malt".
	1.692	1.716	
13	1.129	1.35	20% solution used. Product labeled "A compound of malt, skim milk powder and sugar".
	1.22	1.24	
14	6.74	6.659	....
	6.69	6.629	
15	4.135	3.898	20% solution used. Product chocolate flavored.
	4.16	3.976	
16	0.502	0.526	20% solution used. Product labeled "Compound of malt and milk".
	0.569	....	

RECOMMENDATIONS.

It is recommended—

(1) That the "neutral" procedure, as outlined, be adopted as a tentative method for the determination of fat in malted milk.

(2) That a further study be made of the neutral Roese-Gottlieb method as applied to dried milk products.

MOISTURE IN CHEESE.

A communication received from L. C. Mitchell, Associate Referee, reads as follows:

> "Owing to the large amount of work at this Station your Associate Referee was unable to carry out the collaborative study, as planned, of the present tentative method, with the changes as recommended last year, for the determination of moisture in cheese. It is suggested, however, that a collaborative study of this method be made during the coming year."

RECOMMENDATION.

It is recommended—

That the present tentative method for moisture in cheese, together with changes proposed in the report of the Associate Referee in 1921, be subjected to further collaborative study during the coming year.

DATA SECURED WITH THE "TURBIDITY POINT" OF BUTTER FAT.

By Armin Seidenberg (Chemical Laboratory, Department of Health, New York, N. Y.).

Many of the values used in identifying fats and oils are dependent, not upon properties possessed by the entire substance, but upon some one constitutent that may be present quantitatively in a comparatively slight proportion. Thus, in butter fat, the Reichert-Meissl number is the most characteristic value; but it is dependent upon the presence of a comparatively small quantity of the total fatty acids present, which form only a fraction of the complete butter fat. The volatile fatty acids, upon which the determination of the Reichert-Meissl number depends, are affected by seasonal variations, changes in feed, and other factors to a more marked degree than is the case with other constituents of butter fat. On the other hand, the addition of many foreign fats usually affects all the components of butter fat equally.

The "turbidity point" of butter fat, described by the writer in pre-

vious papers[1], is dependent upon the solubility relationship of the glycerides to each other and to the particular solvents used. It takes into account to some extent properties possessed by all the main constituents of butter fat.

The turbidity point serves to indicate the presence of quantities of certain foreign fats that can not be detected by other values. Some examples of this in work on experimental mixtures made up in the laboratory were given in one of the previous papers[2]. Similar results were also secured on suspected cream samples submitted for analysis.

In order to secure the fat in these creams for examination, a somewhat simplified procedure was devised. After allowing the creams to sour by natural fermentation, about 200 grams were thrown upon a large filter and 25–30 cc. of water were added. After being allowed to drain from 12 to 24 hours, or until the residue had a fairly firm consistency, the filter paper was peeled off and the residue transferred to a small beaker. The room temperature during the draining of the creams should not be much above 20°C. as otherwise the lower-melting-point glycerides of the fat melt and are absorbed by the paper. For this reason, also, the residue should not remain on the filter paper after the water has passed off. The beaker containing the cream residue was placed in an oven at a temperature of 90–100°C., care being taken not to use a temperature that would produce charring. Gradually the fat separated out and, after repeated stirring in order to mix the sample and to permit any water present to evaporate, the fat was poured off through a funnel containing a small wad of absorbent cotton. It was then ready for chemical examination. This method yields an entirely representative sample of fat, but of course it is not quantitative.

The turbidity point was determined on the fat secured in this way from over 1000 samples of cream. The majority of these samples did not give any evidence of adulteration by any of the values determined on them, the turbidity point as well as the other values being normal. In a considerable proportion of other samples, however, evidence of adulteration was indicated either by the turbidity point alone, the other values being normal, or it was definitely confirmed by the turbidity point in cases where other evidence was inconclusive.

In Table 1 certain of these results have been selected as typical of those cases in which the usual values are all practically normal, although the turbidity point is 12 to 26 points beyond the limits of 48 to 64, established for a pure butter fat. There is no doubt that the presence of a foreign fat in these cases can be considered as clearly established by the results obtained by the turbidity point even though not substantiated by any of the other values.

---

[1] *J. Ind. Eng. Chem.*, 1918, **10**: 617; *J. Assoc. Official Agr. Chemists*, 1922, **5**: 512.
[2] *J. Ind. Eng. Chem.*, 1918, **10**: 617.

TABLE 1.

Typical cases where the turbidity point establishes adulteration which escapes detection by other tests.

SAMPLE NO.	REICHERT-MEISSL NO.	POLENSKE NO.	REFRACTIVE INDEX AT 25°C.	TURBIDITY POINT
1	23.0	1.9	1.4623	36
2	27.8	2.2	1.4615	36
3	28.1	1.7	1.4588	34
4	29.3	1.9	1.4583	36
5	22.8	1.6	1.4594	90

In Table 2 the results obtained by the usual values are near the border line of the established limits, and they deviate very little from extreme variations noted on unadulterated butter fat. The turbidity point in these instances, however, is 16 to 19 points beyond the established limits, and the presence of a foreign fat can be considered as decisively established on the basis of the evidence supplied by it. In cases such as these the turbidity point affords a valuable and in some instances, necessary confirmation to the evidence supplied by the other values.

TABLE 2.

Results showing adulteration by turbidity point where other constants are not entirely conclusive.

SAMPLE NO.	REICHERT-MEISSL NO.	POLENSKE NO.	REFRACTIVE INDEX AT 25°C.	TURBIDITY POINT
1	21.9	5.6	1.4575	32
2	23.0	5.2	1.4582	30
3	18.7	3.9	1.4567	30
4	20.3	5.4	1.4583	31
5	17.0	4.2	1.4580	29

In the experience of the writer, it is not possible to add to butter fat any considerable quantity of the more common natural fats or oils, with perhaps one exception, without producing a mixture in which their presence would be indicated by the turbidity point even though not indicated by any of the other values. It may, however, be possible by carefully controlled addition of certain artificial fats or mixtures to destroy the evidence of adulteration supplied by the turbidity point. Other values may or may not in these instances serve to indicate adulteration.

The turbidity point referred to in this paper occurs when certain of the least soluble glycerides are thrown out of solution. It would seem that additional information could be obtained by developing another turbidity point which would serve to throw these glycerides out of solution coming next in the order of solubility. This could be accomplished either by filtering off the precipitate obtained by the first turbidity point and running another turbidity point after the addition of alcohol containing water and of ether, or otherwise by doing this directly

on the original fat after redissolving the precipitate by raising the temperature.

From some experimental work undertaken by the writer but not yet concluded it would seem possible in this way to develop a second and, if necessary, a third turbidity point by which the presence of any foreign fat, natural or artificial, could be established with complete certainty.

REPORT ON FATS AND OILS.

By G. S. Jamieson (Bureau of Chemistry, Washington, D. C.), *Referee.*

In accordance with Recommendations 1 and 2 (1921 report[1]) the referee communicated with the American Society for Testing Materials in regard to the preparation of the Wijs solution in order to secure uniformity in methods authorized by this society and the A. O. A. C. It was found that the American Society for Testing Materials had not yet adopted the Wijs method, but experimental work under the direction of the Linseed Oil Committee is being conducted at the present time with a view to adopting this method ultimately. This society is using the same method for the preparation of the Wijs solution as that given under the official procedure of this association[2]. Investigation has shown that the method of preparing the Wijs solution in general use in this country and abroad (by iodine and chlorine gas in an acetic acid solution) is identical with that given under the official method. This method of preparation, given in many works on the analysis of oils, was adopted April 14, 1919, in the Report of the Committee on Analysis of Commercial Fats and Oils of the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society[3].

The chairman of the Linseed Oil Committee of the American Society for Testing Materials stated that it was his opinion, based upon investigations of other chemists, that the alternative method for the preparation of the Wijs solution using iodine and iodine trichloride in an acetic acid solution was not so satisfactory as the solution made from iodine and chlorine gas. In this connection it is interesting to note that in the 1918 Report on the Tentative Standard Methods for the Sampling and Analysis of Commercial Fats and Oils[4] by the Committee of the American Chemical Society mentioned above, the iodine trichloride method of preparing the Wijs solution was given, while in the 1919 report of this committee, which was adopted as official, the original method for the preparation of this solution was substituted without any comment in the notes and remarks. However, this change showed that the use of iodine trichloride was not satisfactory.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, 5: 512.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 245.
[3] *J. Ind. Eng. Chem.*, 1919, 11: 1161.
[4] *Ibid.*, 1918, 10: 315.

During the years 1918 and 1919 the Bureau of Standards made an investigation of the Wijs method in which solutions prepared by both methods were employed, and it was found that the solutions made with iodine and iodine trichloride were not satisfactory because they gave lower results than those obtained with the solutions prepared from iodine and chlorine gas. It is not surprising that the use of iodine trichloride proved unsatisfactory in view of its unstable nature, and this accounts for the fact that it can not be readily purchased in a pure condition. Soon after the manufacture of iodine trichloride it begins to decompose into iodic acid, iodine, etc. Therefore it is recommended that this alternative method for the preparation of the Wijs solution be not adopted, and further that a statement be inserted in the A. O. A. C. official Wijs method calling attention to the undesirability of using iodine trichloride for the Wijs solution on account of its unstable character.

Under Recommendation 3 (1921 report), that further study of the Hanus method be made as to the length of time of absorption (contact of Hanus solution with oil), a series of experiments was made by W. F. Baughman in the Bureau of Chemistry, and the results given in Table 1 show conclusively that no advantage is gained by allowing the Hanus solution to react with an oil for 45 minutes instead of 30 minutes as stated in the official method. In view of the results obtained it is not considered necessary to undertake collaborative work.

TABLE 1.

Iodine numbers by Hanus method.

OIL	½ HOUR ABSORPTION	¾ HOUR ABSORPTION
Linseed	178.5	177.7
Soya bean	128.7	129.5
Cottonseed	113.8	113.4
Mustard seed	109.1	109.3
Neat's foot	66.7	67.5

As directed, the referee conferred with the American Society for Testing Materials in regard to the preparation of the Hanus solution and found that the A. O. A. C. official method is employed.

In accordance with Recommendation 4 (1921 report) further study was made on the detection of sesame oil in olive oil, special attention being given to those olive oils of African and Spanish origin which themselves give a crimson color with the sesame oil reagents. The referee recommended last year that the testing of the liquid or unsaturated acids of these oils be added to the present official methods because they give no color. Since then two rapid methods for the removal of the color not due to sesame oil have been found. Consequently, this year it is recommended that the testing of the liquid acids for sesame oil be not added to the official methods.

The first method studied was that of Prax[1], which is based on shaking the olive oil with 10 per cent alcoholic ammonia, heating until the ammonia and alcohol are removed, and then applying the usual test. The reports of the collaborators were very satisfactory. However, in view of the fact that the referee's attention subsequently was directed to a modification of the Villavecchia method, which is even simpler than the Prax procedure, none of the results obtained with the Prax method will be given in this report.

The modification referred to was devised or accidentally discovered many years ago in the Bureau of Chemistry by L. M. Tolman and was called to the attention of the referee by C. S. Brinton. The test is made according to the official Villavecchia method, and the color is allowed to develop for 10 minutes before the test solution is shaken with 10 cc. of water. Any color not due to sesame oil disappears at once. Since it was found that when the Baudouin reagent (sugar + hydrochloric acid) was used, the color not due to sesame oil did not completely disappear after shaking with water and further that in many cases the color due to sesame oil faded very fast, it is recommended that the Tolman modification be used only with the Villavecchia reagent (furfural and alcohol).

SAMPLES SENT TO COLLABORATORS.

Five samples of olive oils labeled A, B, C, D, and E were sent to the collaborators. Sample A was a Spanish oil which gave a crimson color with the reagents. Sample B was a mixture of 75 per cent of Spanish oil (A) and 25 per cent of California oil (C). This mixture when first made gave a light crimson color when tested, but after standing several weeks it failed to give the color. Sample C was a California olive oil which gave no color with the reagents. Sample D was California oil (C) containing 5 per cent of sesame oil, while Sample E was Spanish oil (A) with a like amount of sesame oil. In view of the satisfactory results obtained on applying the modified Villavecchia method to these samples, and of the fact that this method has been successfully used by a number of chemists for many years, it is recommended that no further study be made, and that it be made an official method.

Table 2 gives the results obtained and reported by the collaborators.

DISCUSSION.

Although Sample B contained a large amount of Spanish olive oil (75 per cent) and gave at first a pale crimson color with the sesame oil reagents, after standing for two weeks it was found that it did not give any color; this accounts for most of the tests of B being negative.

[1] *Ann. fals.*, 1921, 14: 270.

TABLE 2.

Collaborative results obtained on five oils using four different tests.

ANALYST	OIL	VILLAVECCHIA TEST	TOLMAN MODIFICATION	BAUDOUIN TEST	TOLMAN MODIFICATION
L. W. Ferris, Southern Cotton Oil Co., Savannah, Ga.	A	Positive	Negative		
	B	Negative	Negative		
	C	Negative	Negative		
	D	Positive (strong)	Positive (strong)		
	E	Positive (strong)	Positive (strong)		
H. S. Bailey, Southern Cotton Oil Co., Savannah, Ga.	A	Positive (faint)	Negative	Positive (medium)	Faint pink color
	B	Negative	Negative	Very faint pink	Negative
	C	Negative	Negative	Negative	Negative
	D	Positive (strong)	Positive (medium)	Positive (strong)	Positive (faint)
	E	Positive (strong)	Positive (strong)	Positive (strong)	Positive (faint)
H. P. Strack, Southern Cotton Oil Co., Savannah, Ga.	A	Positive (medium)	Negative	Positive (medium)	Faint pink
	B	Very faint pink	Negative	Very faint pink	Negative
	C	Very faint pink	Negative	Negative	Negative
	D	Positive (strong)	Positive (medium)	Positive (strong)	Positive (faint)
	E	Positive (strong)	Positive (medium)	Positive (strong)	Positive (faint)
I. T. Parsons, H. J. Heinz Co., Pittsburgh, Pa.	A	Positive	Negative	Positive	Faint pink color
	B	Negative	Negative	Negative	Negative
	C	Negative	Negative	Negative	Negative
	D	Positive (strong)	Positive (strong)	Positive	Positive
	E	Positive (strong)	Positive (strong)	Positive	Positive
R. M. Hann, Bureau of Chemistry, Washington, D. C.	A	Positive (crimson)	Negative		
	B	Faint crimson	Negative		
	C	Negative	Negative		
	D	Positive (strong)	Positive (strong)		
	E	Positive (strong)	Positive (strong)		
A. L. Mehring, Bureau of Animal Industry, Washington, D. C.	A			Positive	Negative
	B			Negative	Negative
	C			Negative	Negative
	D			Positive (strong)	Positive
	E			Positive (strong)	Positive
G. S. Jamieson.	A	Positive (crimson)	Negative		
	B	Pale crimson	Negative		
	C	Negative	Negative		
	D	Positive (strong)	Positive (strong)		
	E	Positive (strong)	Positive (strong)		
R. H. Kerr, Bureau of Animal Industry, Washington, D. C.	A			Positive	Faint pink
	B			Negative	Negative
	C			Negative	Negative
	D			Positive (strong)	Positive
	E			Positive (strong)	Positive
I. B. Martin, Bureau of Animal Industry, Washington, D. C.	A			Positive	Faint pink
	B			Negative	Negative
	C			Negative	Negative
	D			Positive (strong)	Positive
	E			Positive (strong)	Positive
D. G. Sorber, Bureau of Animal Industry, Washington, D. C.	A			Positive	Faint pink
	B			Negative	Negative
	C			Negative	Negative
	D			Positive (strong)	Positive
	E			Positive (strong)	Positive

Since it was recommended that a more comprehensive description be prepared in connection with the tests for sesame oil, the following is offered for consideration:

SESAME OIL.

Baudouin Test.–Official.

Dissolve 0.1 gram of finely powdered sugar in 10 cc. of hydrochloric acid (sp. gr. 1.2), add 10 cc. of the oil to be tested, shake thoroughly for 1 minute and allow to stand for 10 minutes. In the presence of even a very small admixture of sesame oil, the aqueous

solution is colored crimson. It should be observed that some olive oils, especially those of African or Spanish origin, give pink or crimson colors which can be readily differentiated from the color due to sesame oil by applying the following modification of the Villavecchia method:

Villavecchia Test.

Add 2 cc. of furfural to 100 cc. of 95 per cent alcohol by volume and mix thoroughly 0.1 cc. of this solution with 10 cc. of hydrochloric acid (sp. gr. 1.2) and 10 cc. of the oil to be tested by shaking them together for ¼ of a minute. Allow mixture to stand 10 minutes, observe color, add 10 cc. of water, shake and again observe color. If the crimson color disappears, sesame oil is not present.

NOTE.—As furfural gives a violet tint with hydrochloric acid, it is necessary to use the very dilute solution specified above.

FUTURE WORK.

THE DETERMINATION OF UNSAPONIFIABLE MATTER.

The Fat and Oil Committee of the American Chemical Society requested the referee to call attention to the fact that the association's official method for unsaponifiable residue which was adopted years ago was not found satisfactory by the committee. The reason why it is mentioned at this time is that the A. O. A. C. methods are recognized abroad, and a number of referee chemists have stated that they are using the methods which, with this one exception, would be recognized as suitable for commercial referee work. It was stated that the method given in the last report of the Committee on Standard Methods for the Sampling and Analysis of Commercial Fats and Oils[1], based on several years' study and a large amount of cooperative work, was found to give very desirable results. Since the determination of unsaponifiable matter is very important commercially, it was requested by the committee that this association take up again the study of this determination.

The attention of the referee was called by R. Hertwig and T. O. Kellems to an important omission in the description of the official method for the preparation of the Hanus solution[2], which is liable to cause some chemists to make serious errors in the preparation and standardization of this solution.

The method should be corrected as follows:

The sentence beginning "Add 3 cc. of bromine to 200 cc. of acetic acid, etc.", should read "Add 3 cc. of bromine to 200 cc. of acetic acid and titrate 5 cc. of the solution against the N/10 sodium thiosulfate, adding 10 cc. of potassium iodide solution (15%) before titrating".

RECOMMENDATIONS.

It is recommended—

(1) That the alternative method for the preparation of the Wijs solution (iodine trichloride method) be not adopted, and further that a

[1] *J. Ind. Eng. Chem.*, 1919, 11: 1161.
[2] *Assoc. Official Agr. Chemists Methods*, 1920, 244, par. (a).

statement be inserted in the A. O. A. C. official Wijs method[1] calling attention to the undesirability of using iodine trichloride for the Wijs solution on account of its unstable character.

(2) That the method for the preparation of the Hanus solution be corrected as specified in this report, but that no other change be made in the official Hanus method.

(3) That the modified Villavecchia test be made official. It is recommended also that the description of the Baudouin and modified Villavecchia tests be changed to read as given in this report.

(4) That further work be done on the determination of the unsaponifiable matter.

H. S. Bailey: It is apparently difficult to obtain hydrochloric acid which has a specific gravity of 1.20, as recommended in the present official method for the detection of sesame oil in olive oil.

It has been found that acid with a specific gravity of 1.18 is just as satisfactory as the stronger acid in this test, and therefore it is suggested that when the present method is rewritten hydrochloric acid of 1.18 specific gravity be specified.

It was recommended by Committee B that a study be made of the Baudouin and Villavecchia tests using hydrochloric acid of varying specific gravity.

REPORT ON BAKING POWDER.

By L. H. Bailey (Bureau of Chemistry, Washington, D. C.), *Referee.*

The work on baking powder for 1922 was followed along the lines recommended by Committee C at the 1921 meeting. Collaborative work was done on the electrolytic determination of lead, the neutralizing value of mono-calcium phosphate, the volumetric determination of carbon dioxide and the determination of fluorine.

The samples sent to the collaborators were prepared through the courtesy of J. R. Chittick, Jaques Manufacturing Co., Chicago, Ill.; E. W. Thornton, R. B. Davis Co., Hoboken, N. J.; and Augustus H. Fiske, Rumford Chemical Works, Providence, R. I.

DETERMINATION OF LEAD BY THE ELECTROLYTIC METHOD.

Directions:

(1) Use the Corper-Bryan method as published[2].

(2) Use your own method, giving with your report the details of the method used.

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 245.
[2] *J. Assoc. Official Agr. Chemists*, 1920, 4: 221.

Samples for the determination of lead were sent to 10 analysts who had agreed to work along this line, but results were received from only two of them, and these results are so widely apart that they are worthless. It is possible that in the case of one analyst a mistake was made in placing the decimal point. The following are the results submitted:

TABLE 1.
Electrolytic determination of lead.

ANALYST	BRYAN-CORPER METHOD	ANALYST'S METHOD
	parts per million	*parts per million*
Augustus H. Fiske	4.1	6.6
	5.2	8.0
Average.............	4.7	7.3
J. K. Morton, Bureau of Chemistry, Washington, D. C.	57.69	
	62.80	
	58.90	
Average.............	59.80	

More work should be done with this method or with modifications of it before taking any action as to its adoption.

NEUTRALIZING STRENGTH OF MONO-CALCIUM PHOSPHATE.

The use of different indicators and combinations of indicators was studied by Ruth Buchanan of the Food Control Laboratory of the Bureau of Chemistry, but the subject was not submitted to collaborative study. Her report on this subject follows:

In the study of the use of different indicators the following method was employed:

0.84 gram of the phosphate was weighed and put into a 250 cc. beaker; 125 cc. of distilled water and a definite amount of a standard indicator solution were added. The solution was titrated with 0.5N nitric acid until the proper end-point was obtained, and then boiled for 1 minute. The titration was continued where necessary to regain the correct end-point. The total reading multiplied by 5, equals the neutralizing value in terms of parts sodium bicarbonate per 100 parts of phosphate.

The indicators used were:

(1) Phenolphthalein	0.5% alcoholic solution
(2) Thymolphthalein	0.04% alcoholic solution
(3) Thymol Blue	0.04% solution.
(4) Methyl Red	0.02% alcoholic solution.

These indicators were suggested by an article by J. L. Lizius[1].

A starch-filled phosphate was used in this work.

The results obtained are given in Tables 2, 3, and 4.

[1] *Analyst*, 1921, 46: 355.

TABLE 2.

Titration.

	COLD 0.5N SODIUM HYDROXIDE	HOT 0.5N SODIUM HYDROXIDE	NEUTRALIZING VALUE
	cc.	*cc.*	
1 cc. Phenolphthalein	8.9	8.9	44.5
1 cc. Thymolphthalein	9.75	10.2	51.0
0.25 cc. Phenolphthalein 0.75 cc. Thymolphthalein	9.2	9.2	46.0
0.5 cc. Phenolphthalein 0.5 cc. Thymolphthalein	9.1	9.1	45.5
0.4 cc. Phenolphthalein 0.6 cc. Thymolphthalein	9.02	9.02	45.10
1 cc. Phenolphthalein 3 cc. Thymolphthalein	9.05	9.05	45.25
0.75 cc. Phenolphthalein 0.25 cc. Thymolphthalein	8.95	8.95	44.75
0.6 cc. Phenolphthalein 0.4 cc. Thymolphthalein	8.95	8.95	44.75
3 cc. Phenolphthalein 1 cc. Thymolphthalein	8.60	8.60	43.00

All the above combinations work well.

TABLE 3.

Titration.

	COLD 0.5N SODIUM HYDROXIDE	HOT 0.5N SODIUM HYDROXIDE	NEUTRALIZING VALUE	REMARKS
	cc.	*cc.*		
1 cc. Methyl Red	1.1	4.4	22.0	End-point fair.
1 cc. Thymol Blue	9.7	9.7	48.5	End-point good.
0.25 cc. Methyl Red 0.75 cc. Thymol Blue	9.3	9.7	48.5	Orange color to start, yellow with 3 cc. alkali, blue with 9.3 cc. alkali.

The combination of methyl red and thymol blue is no better than thymol blue by itself.

TABLE 4.

Titration.

	COLD 0.5N SODIUM HYDROXIDE	HOT 0.5N SODIUM HYDROXIDE	NEUTRALIZING VALUE
	cc.	*cc.*	
0.5 cc. Thymol Blue, 1 drop Methyl Orange..........................	9.7	9.7	48.5
1 cc. Methyl Orange.................	0.1	0.1	0.5

Methyl orange gives too low results. A combination of methyl orange and thymol blue is no better than thymol blue by itself.

CONCLUSIONS.

(1) Of all the indicators employed, the combination of phenolphthalein and thymolphthalein is preferred. The best proportion probably is half and half. The end-point obtained by the use of both indicators is a little more distinct than that obtained by the use of either one alone.

(2) The indicator should be made up with accuracy, and the amount should be measured by means of a pipet graduated in tenths of a cc.

Collaborative study was made of the neutralizing value of mono-calcium phosphate by using two methods sent out by the referee as follows:

NEUTRALIZING VALUE OF MONO-CALCIUM PHOSPHATE.

Method I.

Weigh 0.84 gram of phosphate into a 3A casserole.

Add 25 cc. of water and stir a moment.

Add exactly 90 cc. of 0.1N sodium hydroxide.

Bring to boil and boil for 1 minute.

Add 1 drop of phenolphthalein (1% solution).

Titrate while still boiling hot with 0.2 hydrochloric acid.

End-point when pink color due to indicator has all but disappeared and does not return in one minute.

CALCULATION.

$90-2\times$ (cc. standard hydrochloric acid used) = neutralizing strength of 100 parts of phosphate in terms of bicarbonate of soda.

Method II.

Weigh 0.84 gram of mono-calcium phosphate into a 150 cc. beaker.

Add 25 cc. of water and 10–15 drops of phenolphthalein (1% solution).

Titrate with 0.5N sodium hydroxide to a faint pink, then heat to boiling, boil 1 minute and titrate while hot to faint pink again.

(Add bulk of alkali rapidly with vigorous stirring.)

CALCULATION.

Total buret reading $\times$ 5 = neutralizing strength of 100 parts of phosphate in terms of bicarbonate.

These methods are so different that the results obtained were noticeably lower in one case than in the other. The collaborators were asked to make up baking powders with the sample of phosphate sent them by adding the amount of bicarbonate of soda indicated by their determinations and then make biscuits with these baking powders and report upon the character of the biscuits made.

Table 5 gives the average results of the collaborators using the two methods suggested.

DISCUSSION.

The analysts in commenting upon the biscuits made as directed were in agreement that there was not a great difference but that those made as indicated by Method II were whiter in color than those made according

TABLE 5.

Neutralizing value of mono-calcium phosphate.

ANALYST	METHOD I	METHOD II	RUMFORD METHOD*
	per cent	*per cent*	*per cent*
Augustus H. Fiske	82.20	72.00	71.40
W. G. Warning, Provident Chemical Works, St. Louis, Mo.	79.90	73.00	....
A. L. Foscue, Piedmont Electric Chemical Co., Mt. Holly, N. C.	81.675	79.50	....
R. Leone Rutledge, Bureau of Chemistry, Washington, D. C.	81.09	71.25	....
Ruth Buchanan	79.74	71.25	....

*Similar to Method II.

to the proportions given in Method I. On the other hand, there was no evidence of undecomposed bicarbonate of soda in the biscuits made according to results obtained by Method I.

Experiments made in the Food Control Laboratory of the Bureau of Chemistry showed that a greater proportion of phosphate than indicated by Method II did not increase the whiteness of the biscuits, while a greater proportion of bicarbonate of soda than indicated by Method I did give a yellow biscuit, the color of which became more intense with increasing amounts of soda.

It is the opinion of the referee that the results obtained by Method II are more nearly in accord with those that are actually obtained in baking than are the results by Method I, and that those obtained by Method I are too high for exact neutrality in baked goods although they are not so high but that these figures may be used in making up baking powder that will produce biscuits which do not give evidence of containing an excessive amount of soda. Quite a range may exist, therefore, within which a value may be taken as the neutralizing value and used satisfactorily in calculating the proportions to be employed in making a baking powder. Nevertheless it would be desirable to have one method only for getting the neutralizing value, and this should represent as nearly as possible the reaction actually obtained in baking. For this reason Method II is suggested as the more desirable method.

FLUORINE IN BAKING POWDER.

This phase of the subject was handled by J. K. Morton, the associate referee, and a report will be made by him.

VOLUMETRIC METHODS FOR THE DETERMINATION OF CARBON DIOXIDE.

Two methods for the volumetric determination of carbon dioxide in baking powders were studied. Descriptions of these methods were fur-

nished by the firms originating them. They have been used for a number of years for routine control work and this year were submitted to collaborative study. The methods are as follows:

A simple and rapid volumetric method for the estimation of carbon dioxide in baking powder.

(Submitted by R. B. Davis Co., Hoboken, N. J.)

The apparatus consists of a Schiff nitrometer (Eimer & Amend No. 4750) graduated to 100 cc. in 1/5 cc. with the adapter tube (B) sealed off about one inch from the nitrometer tube. A leveling bulb (D) is attached to the nitrometer tube at C by means of heavy rubber tubing (E), of sufficient length to allow the leveling bulb to be raised to the top of the nitrometer tube.

To the top of the nitrometer tube above the stop-cock (F), which should be left open at all times, is attached another piece of heavy rubber tubing, the other end of which is attached to a piece of strong glass tubing of about 5/16 inch inside diameter passing through a No. 9 rubber stopper (G).

The rest of the apparatus consists of (1) a heavy glass bottle cap (the same as used for covering stoppers) of 1⅝ inches diameter and having a capacity of about 50 cc. and (2) a flat-bottomed glass cylinder (J), having an inside diameter of 11/16 inch and height of 1⅛ inches, with a 5 cc. graduation marked about 3/16 inch from the top. (This cylinder may be made by cutting off a flat-bottomed test tube of 11/16 inch diameter, 1⅛ inches from bottom of the tube.)

The nitrometer tube should be filled with mercury, care being taken that air bubbles are expelled. The leveling bulb should be about half filled with mercury when the bulb is raised to the top of the nitrometer tube. The apparatus should be supported on a ring stand having a heavy base by two strong clamps.

DETERMINATIONS.

0.5 gram of the well-mixed sample is introduced into the bottom of the glass bottle cap (H). 5 cc. of hydrochloric acid (sp. gr. 1.127) is placed in the cylinder (J), which should be absolutely dry on the outside, and the cylinder lowered into the bottom of the bottle cap (H) by holding it against the side of the bottle cap by the index finger. The bottle cap is then connected with the rubber stopper (G), care being taken not to overturn or shake out any of the acid on the sample of baking powder. (The leveling bulb should be near the top of the nitrometer tube when this connection is made.)

The level of the mercury in the leveling bulb and in the nitrometer tube is then adjusted so that the levels are exactly the same and the reading taken. Then holding the cup (H) in the right hand and the leveling bulb in the left, shake the cup, overturning the acid on the sample. The level of the mercury in the nitrometer tube will fall. Lower the leveling bulb with the left hand, keeping the levels of the mercury in the bulb and in the tube as nearly the same as possible during the entire evolution of the gas.

Shake the cup (H) thoroughly in order to be sure that all the baking powder has been decomposed, adjust the levels of the mercury in the leveling bulb and in the nitrometer tube by moving the leveling bulb up and down an inch or so until the levels are again exactly the same, and take the reading. Note temperature and pressure.

The per cent of carbon dioxide is calculated as follows:

Example:	Volume of gas liberated..................	35.0 cc.
	Temperature............................	29°C.
	Barometer..............................	760 mm.

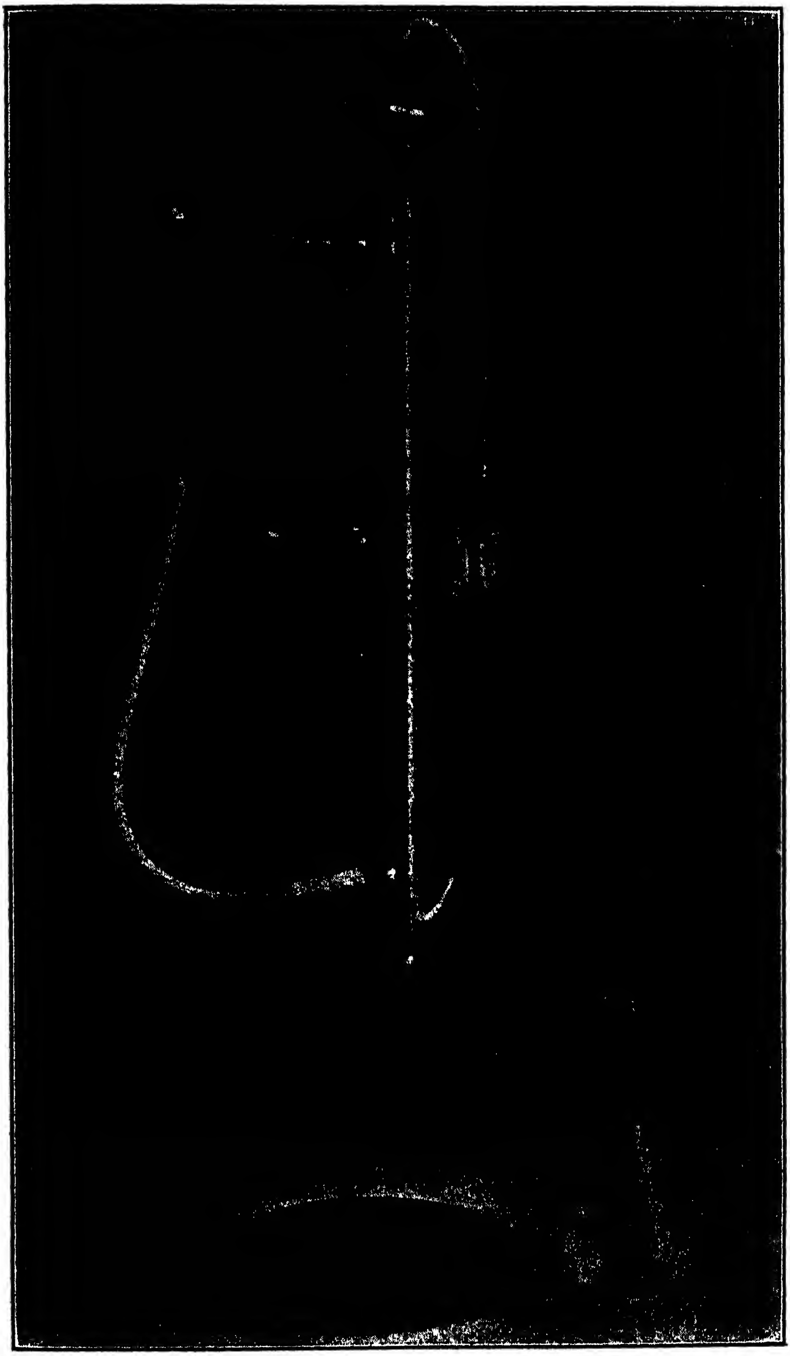


FIG. 1.—ABSORPTION APPARATUS FOR DAVIS METHOD

From Table 6, absorption of carbon dioxide in 5 cc. of hydrochloric acid (sp. gr. 1.127) is 5.16 cc.

Therefore, total evolution of gas is 35.0+5.16 cc. = 40.16 cc.

From Table 7, weight of 1 cc. of carbon dioxide (in milligrams) at 29°C. and 760 mm. pressure = 1.7101.

$$1.7101 \times 40.16 = 0.0686 \text{ gram.}$$

$$0.0686 \times 2 \times 100 - 0.25^{1} = 13.47\% \text{ carbon dioxide.}$$

TABLES TO BE USED WITH THE DAVIS METHOD.

TABLE 6.

Baking powder absorption of carbon dioxide in 5 cc. of hydrochloric acid, sp. gr. 1.127.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	Evolved
1.85	2.00	2.16	2.31	2.47	2.62	2.78	2.93	3.09	3.24	3.40	3.55	3.71	3.86	Absorbed
15	16	17	18	19	20	21	22	23	24	25	26	27	28	Evolved
4.02	4.17	4.33	4.48	4.61	4.79	4.95	4.97	4.98	5.00	5.03	5.04	5.06	5.06	Absorbed
29	30	31	32	33	34	35	36	37	38	39	40	41	42	Evolved
5.07	5.09	5.10	5.11	5.13	5.14	5.16	5.17	5.18	5.20	5.21	5.23	5.24	5.25	Absorbed
43	44	45	46	47	48	49	50	51	52	53	54	55	56	Evolved
5.26	5.27	5.28	5.30	5.31	5.32	5.34	5.35	5.36	5.37	5.38	5.40	5.41	5.42	Absorbed
57	58	59	60	61	62	63	64	65	66	67	68	69	70	Evolved
5.44	5.45	5.47	5.48	5.50	5.51	5.52	5.54	5.55	5.57	5.58	5.59	5.61	5.62	Absorbed
71	72	73	74	75	76	77	78	79	80	81	82	83	84	Evolved
5.64	5.65	5.66	5.68	5.69	5.71	5.72	5.73	5.75	5.76	5.78	5.79	5.80	5.82	Absorbed
85	86	87	88	89	90	91	92	93	94	95	96	97	98	Evolved
5.83	5.85	5.86	5.87	5.89	5.90	5.92	5.93	5.94	5.96	5.97	5.99	6.00	6.02	Absorbed
99	100													Evolved
6.03	6.04													Absorbed

TABLE 7.

Weight of a cc. of carbon dioxide in milligrams.

(Millimeter on barometer.)

756	758	760	762	764	766	768	770	772	774	°C.
1.8399	1.8448	1.8498	1.8548	1.8597	1.8647	1.8697	1.8748	1.8798	1.8848	13
1.8318	1.8367	1.8417	1.8466	1.8515	1.8565	1.8614	1.8663	1.8713	1.8763	14
1.8233	1.8292	1.8331	1.8381	1.8430	1.8479	1.8528	1.8577	1.8626	1.8675	15
1.8150	1.8199	1.8248	1.8297	1.8346	1.8395	1.8444	1.8492	1.8541	1.8590	16
1.8065	1.8114	1.8162	1.8211	1.8260	1.8308	1.8357	1.8406	1.8454	1.8503	17
1.7981	1.8030	1.8078	1.8127	1.8175	1.8233	1.8282	1.8330	1.8379	1.8427	18
1.7895	1.7943	1.7992	1.8040	1.8089	1.8137	1.8185	1.8234	1.8282	1.8331	19
1.7309	1.7857	1.7906	1.7954	1.8002	1.8050	1.8099	1.8147	1.8195	1.8243	20
1.7722	1.7770	1.7818	1.7866	1.7914	1.7962	1.8012	1.8060	1.8108	1.8156	21
1.7634	1.7682	1.7730	1.7778	1.7326	1.7874	1.7922	1.7970	1.8018	1.8066	22
1.7546	1.7593	1.7641	1.7689	1.7737	1.7784	1.7882	1.7880	1.7928	1.7975	23
1.7456	1.7503	1.7551	1.7598	1.7647	1.7694	1.7741	1.7788	1.7836	1.7884	24
1.7365	1.7412	1.7460	1.7507	1.7554	1.7602	1.7649	1.7697	1.7744	1.7791	25
1.7274	1.7321	1.7368	1.7416	1.7463	1.7510	1.7557	1.7605	1.7652	1.7699	26
1.7184	1.7231	1.7278	1.7325	1.7372	1.7419	1.7466	1.7513	1.7660	1.7707	27
1.7094	1.7142	1.7189	1.7232	1.7283	1.7330	1.7378	1.7427	1.7474	1.7517	28
1.7016	1.7054	1.7101	1.7148	1.7199	1.7241	1.7298	1.7345	1.7382	1.7429	29
1.6920	1.6967	1.7014	1.7051	1.7107	1.7153	1.7190	1.7246	1.7293	1.7339	30

NOTE.—A correction factor must be determined for each apparatus. 0.25 will be found to be about right.

A volumetric method and apparatus for determining the carbon dioxide content of baking powder.

(Submitted by J. Raymond Chittick.)

DETERMINATION.

The determination is carried out in an apparatus by treating a factor weight of the baking powder, or the residue therefrom, with dilute sulfuric acid and measuring the volume of the evolved carbon dioxide.

APPARATUS.

The apparatus consists of a decomposition flask connected by means of a glass T-tube, provided with a stop-cock, to a gas measuring tube, which in turn is connected to a leveling bulb. The composition flask—a 250 cc. Pyrex wide-mouth extraction flask—is fitted with a two-hole rubber stopper to allow for connection with the gas-measuring tube by means of glass and rubber tubing and for the insertion of the tip of a buret. The buret has a capacity of 25 cc. and is graduated in cubic centimeters at 200°C., numbering each 5 cc. The tip of the buret is extra long, bent in order to pass through the rubber stopper. The gas-measuring tube is graduated in cubic centimeters at 20°C., numbering each 10 cc., the zero mark being placed at a volume of 25 cc. below the top marking to allow for graduating upward from 0 to 25 cc. and downward from 0 to 200 cc.

A rubber connection is made between the glass tube leading from the decomposition flask and the T-tube extensions of the gas-measuring tube to permit the rotation of the decomposition flask. The gas-measuring tube is connected by means of rubber tubing with a leveling bulb. The bulb has a capacity of about 300 cc. A saturated solution of sodium chloride is prepared to which a small amount of sodium bicarbonate is added. The whole is then rendered slightly acid with sulfuric acid. This solution is used in the gas measuring tube and leveling bulb and seldom needs to be replaced.

FIG. 2.—ABSORPTION APPARATUS FOR CHITTICK METHOD.

REAGENT.

Dilute sulfuric acid, sp. gr. 1.14 (approximately one volume of concentrated acid to five volumes of water). This solution is used in the 25 cc. buret.

PREPARATION OF SAMPLE.

Remove the entire sample from the package, pass through a 40-mesh sieve and mix thoroughly.

DETERMINATION.

Thermometric and barometric readings, preferably expressed in degrees Centigrade and in millimeters of mercury, are essential. The factor weight of the baking powder to be used in the determination is dependent upon the existing atmospheric conditions. After both temperature and pressure of the air in the room are determined, reference is made to Parr's table[1] for the density of carbon dioxide, and the weight of *one liter* of carbon dioxide under like conditions is taken as the factor weight.

For example: Pressure = 746 mm.; temperature = 22°C.; one cc. of CO_2 weighs 1.7390 mg. or one liter weighs 1.7390 grams; therefore, 1.7390 grams is the factor weight of baking powder to be taken for analysis.

TOTAL CARBON DIOXIDE.

The factor weight of baking powder is placed in the dry decomposition flask and connection made to the apparatus by means of a rubber stopper. The T-tube stop-cock is opened and, by means of the leveling bulb, the salt solution is brought to a graduation above the zero mark equal in volume to the amount of acid to be used in the decomposition. (For example, if 10 cc. of acid are to be used, the solution is leveled at the 10 cc. graduation above the zero mark.)

A minute is allowed to insure equalization of the temperature and pressure within the apparatus with that in the room.

The stop-cock is closed. The leveling bulb is lowered somewhat, diminishing the pressure within the apparatus, and 10 cc. of dilute acid are slowly run into the decomposition flask. The salt solution should at all times during the decomposition be kept at a lower level than that in the gas-measuring tube to prevent the liberated carbon dioxide from escaping through the acid buret into the air. The decomposition flask is well rotated to secure intimate contact of materials, then allowed to remain at rest for 5 minutes.

The pressure is equalized by means of the leveling bulb and the volume of the evolved gas is read. Divide the number of cc. by 10 to obtain the per cent of total carbon dioxide by weight.

RESIDUAL CARBON DIOXIDE.

The factor weight of baking powder is placed in the decomposition flask; 20 cc. of water are added and allowed to stand 20 minutes. Place the flask in a metal drying cell surrounded by boiling water and heat, with occasional shaking, for 20 minutes. To complete the reaction, heat quickly to boiling and boil for a minute. Cool to room temperature, then connect flask to the apparatus and determine the carbon dioxide present, by treating with 10 cc. of dilute acid as described under total carbon dioxide.

AVAILABLE CARBON DIOXIDE.

Subtract the residual carbon dioxide from the total.

Unfortunately the different analysts did not have both types of volumetric apparatus, but some of them compared the results obtained with one apparatus with those obtained by some other method in use in the laboratory and in general got concordant results.

---

[1] Van Nostrand's Chemical Annual, Olsen, Fourth Issue, 1918, 100.

Two samples for the determination of carbon dioxide were submitted. One of them contained theoretically 16.197 per cent and the other one 13.09 per cent of carbon dioxide. The collaborative results are given in Table 8.

These results are very encouraging and indicate that volumetric methods should be checked against the absorption methods which are now official.

TABLE 8.

Volumetric determinations of carbon dioxide.*

ANALYST	CHITTICK METHOD		DAVIS METHOD		ROBINSON METHOD		RUMFORD METHOD	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
G. D. Richards,	16.15	12.97	....	....	....	....	....	....
Jaques Mfg. Co.	16.15	12.81	....	....	....	....	....	....
Chicago, Ill.	16.13	12.90	....	....	....	....	....	....
	16.14	12.95	....	....	....	....	....	....
	16.16	12.86	....	....	....	....	....	....
	16.16	12.93	....	....	....	....	....	....
Average......	16.15	12.90	....	....	....	....	....	....
J. R. Chittick	16.12	13.05	....	....	....	....	....	....
	16.17	13.05	....	....	....	....	....	....
	....	13.05	....	....	....	....	....	....
Average......	16.15	13.05	....	....	....	....	....	....
C. J. Preston,	16.10	12.93	....	....	....	....	....	....
Jaques Mfg. Co.,	16.15	12.95	....	....	....	....	....	....
Chicago, Ill.	16.10	12.85	....	....	....	....	....	....
	16.10	12.99	....	....	....	....	....	....
	....	12.93	....	....	....	....	....	....
Average......	16.11	12.93	....	....	....	....	....	....
Ruth Buchanan	16.24	13.13	....	13.00	....	....	....	....
	16.15	13.13	....	13.16	....	....	....	....
	16.24	13.13	....	12.93	....	....	....	....
	16.20	13.13	....	13.03	....	....	....	....
	16.14		....	13.06	....	....	....	....
	16.14	Av. 13.13	....	13.03	....	....	....	....
	16.14	....	....	13.06	....	....	....	....
	16.23	....	....	13.06	....	....	....	....
	16.23	....			....	....	....	....
			Average	13.04				
Average......	16.19	....			....	....	....	....
O. B. Winter, Michi-	....	....	16.44	13.46	....	....	....	....
gan Agricultural	....	....	16.30	13.40	....	....	....	....
College, E. Lan-	....	....	16.28	13.46	....	....	....	....
sing, Mich.	....	....	16.34	13.50	....	....	....	....
Average......	....	....	16.34	13.45	....	....	....	....

*Sample No. 1 contained theoretically 16.197% and Sample No. 2, 13.09% of carbon dioxide.

TABLE 8—*Continued.*

Volumetric determinations of carbon dioxide.*

ANALYST	CHITTICK METHOD		DAVIS METHOD		ROBINSON METHOD		RUMFORD METHOD	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
L. J. Hendryx, Michigan Agricultural College, E. Lansing, Mich.	....	....	16.26	13.08	....	....	....	....
	....	....	16.20	12.94	....	....	....	....
	....	....	16.00	13.20	....	....	....	....
	....	....	16.34	13.20	....	....	....	....
	....	....	16.20	13.14	....	....	....	....
	....	....	16.20	12.84	....	....	....	....
	....	....	——	13.00.	....	....	....	....
	....	Average	16.20	12.84	....	....	....	....
	....	....	....	12.94	....	....	....	....
	....	....	....	13.14	....	....	....	....
	....	....	....	13.14	....	....	....	....
	....	....	....	13.08	....	....	....	....
	....	....	....	——	....	....	....	....
	....	....	Average	13.04	....	....	....	....
C. S. Robinson, Michigan Agricultural College, E. Lansing, Mich.	....	....	....	....	16.05	12.76	....	....
	....	....	....	....	16.10	12.82	....	....
	....	....	....	....	16.15	12.67	....	....
	....	....	....	....	16.12	13.03	....	....
	....	....	....	....	16.05	13.00	....	....
	....	....	....	....	——	13.06	....	....
	....	....	....	Average	16 09	12.89	....	....
	....	....	....	....	....	12.75	....	....
	....	....	....	....	....	12.71	....	....
	....	....	....	....	....	12.78	....	....
	....	....	....	....	....	13.05	....	....
	....	....	....	....	....	12.88	....	....
	....	....	....	....	....	——	....	....
	....	....	....	....	Average	12.87	....	....
Augustus H. Fiske	....	....	16.52	13.21	....	....	16.13	13.21
	....	....	16.91	13.31	....	....	16.11	13.21
	....	....	16.26	13.31	....	....	16.11	13.21
	....	....	16.59	——	....	....	——	——
	....	....	16.12	Av. 13.31	....	....	16.12	13.21
	....	....	16.33	....	....	....	....	....
	....	....	16.63	....	....	....	....	....
	....	....	16.49	....	....	....	....	....
	....	....	16.41	....	....	....	....	....
	....	....	——	....	....	....	....	....
	....	Average	16.47	....	....	....	....	....

*Sample No. 1 contained theoretically 16.197 % and Sample No. 2, 13.09 % of carbon dioxide.

RECOMMENDATIONS.

It is recommended—

(1) That the electrolytic method for the determination of lead be further studied.

(2) That Method II for determining the neutralizing value of monocalcium phosphate as collaboratively studied in 1922 be made a tentative method.

(3) That the accuracy of the volumetric methods for the determination of carbon dioxide be compared with the official absorption methods before they are recommended as tentative methods.

REPORT ON FLUORIDES IN BAKING POWDER.

By J. K. MORTON (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*

The report of the associate referee in 1921 pointed out that the Wagner-Ross method for the determination of fluorides as published[1] did not give the degree of accuracy desired when applied to baking powder. Some changes were suggested in the manipulation and apparatus which resulted in a higher and more consistent recovery of fluorine. In the absence of any published detailed instructions as to the procedure in determining fluorine in baking powder a detailed method was submitted for approval.

The report of Subcommittee C recommended that the Wagner-Ross method for fluorine in baking powder be submitted to further study. In accordance with this recommendation samples of baking powder were prepared for collaborative work.

These samples, together with a copy of the Wagner-Ross method and a statement of the experience of the associate referee with this method, setting forth the changes suggested in the report of the associate referee for 1921, were sent to those who had agreed to collaborate in this work. Directions were also given for the preparation of a carbon-free ash.

The collaborators were directed to carry out the determination as follows:

Ash 20 grams of baking powder in a muffle furnace. Place the ash, together with 1 gram of quartz flour and 5 grams of anhydrous copper sulfate, in the digestion flask. Thoroughly mix the contents of the flask. Connect the flask in its position in the train. Pour 50 cc. of special sulfuric acid into the 50 cc. Erlenmeyer flask and place it in its position in the train. Start the air very slowly, tilting the digestion flask sufficiently to allow the first portion of the acid to flow into the trap and form a seal. Regulate the flow of air to give just enough headway to prevent any back pressure. Apply heat to the digestion flask slowly, allowing the mixture to come to boiling in not less than two hours. Shake the flask occasionally during the heating. Boil for ten minutes, remove the flame and allow the air to pass through for thirty minutes longer. Disconnect the delivery tube with the absorption flask and transfer the contents to a 750 cc. Erlenmeyer. Dilute with water to 250 cc., bring to boiling for 10 minutes, cool slightly under running water and titrate with 0.1N alkali, using phenolphthalein as indicator.

The following table gives a record of the results submitted by the collaborators on the determination of fluorine in baking powder:

[1] *J. Ind. Eng. Chem.*, 1917, 9: 1116.

The determination of fluorine in baking powder by the Wagner-Ross method.

IDENTIFICATION NO.	DESCRIPTION OF SAMPLE	FLUORINE ADDED	FLUORINE CALCULATED	J. K. MORTON		A. J. FISKE		L. N. SUTHERS‡§		A. AWOTIN§	W. B. STOKES†	
				Found	Average	Found	Average	Found	Average	Found	Found	Average
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
1	Alum phosphate baking powder as prepared by a commercial firm.	none		0.0199 0.0223 0.0231 0.0190 0.0194 0.0228* 0.0237*	0.0207	0.063 0.054	0.0585	0.116 0.123	0.119	0.124	0.027 0.024	0.026
2	Same powder as No. 1+1.3260 grams of calcium fluoride to 1500 grams of baking powder. Approximately 0.04% fluorine.	0.0430	0.0637	0.0565 0.0603 0.0565 0.0522 0.0596* 0.0635*	0.0551	0.040 0.032	0.0360	0.049 0.048	0.0485	0.437	0.080 0.069	0.075
3	Same powder as No. 1 + 2.6520 grams of calcium fluoride to 1500 grams of baking powder.	0.08605	0.1067	0.0988 0.0883 0.0894 0.0960 0.1045* 0.1026*	0.0931	0.093 0.070	0.0815	0.097 0.100	0.0985	0.0731	0.123 0.126	0.125
4	A straight phosphate baking powder prepared fresh by a commercial firm.	none		0.0104 0.0133 0.0152 0.0128 0.0142* 0.0166* 0.0205*	0.0129	0.017 0.011	0.0140	0.049 0.053	0.051	0.0318	0.022 0.029	0.026

*Ashed with 40% solution of nitrate of magnesia. Not included in average.
†Per cent of fluorine found times the factor 1.117.
‡Magnesium carbonate added to ash.
§Victor Chemical Co.

DISCUSSION AND COMMENTS.

W. E. Stokes of the Royal Baking Powder Company introduced a modification in the manipulation of the method and the calculation of fluorine. He disregarded the production of sulfate in the absorption flask but determined the amount as barium sulfate and corrected accordingly. By a number of control determinations he established a factor of 1.117 for fluorine. His results are very good comparatively, but they are a trifle high.

A. H. Fiske of the Rumford Chemical Company commented on the difficulty of securing a suitable ash by simple ignition and leaching with water. In ashing the material he used a 40 per cent solution of magnesium nitrate. Milk of lime was added to each sample before ignition to be sure there was sufficient base present to prevent the volatilization of fluorine.

L. D. Mathias of the Victor Chemical Company mentioned the difficulty of securing a suitable ash and the importance of a source of constant air pressure. He suggested the use of compressed carbon dioxide because of its general availability, as a carrier for the gases evolved.

The use of magnesium nitrate in ashing the material was given a thorough trial by the associate referee with most excellent results. Duplicate determinations were made on all the collaborative samples with the results reported in the table. The advantage of the use of magnesium nitrate to ash the material was at once apparent. Where carbon is present, the sulfur dioxide evolved by the decomposition of the sulfuric acid is not retained in the chromic sulfuric acid wash solution, except in very slight amounts, but passes on into the absorption tube, introducing a source of error. The addition of magnesium nitrate to the ash and the re-ignition of the material completely destroys the carbon remaining and yields a carbon-free ash. The presence of nitrates in the digestion flask gives rise to nitrous fumes. In passing through the chromic-sulfuric acid wash solutions these are completely absorbed. Repeated tests were made to detect their presence in the absorption tube without success.

The addition of any neutralizing agent to a phosphate or alum-phosphate baking powder before ignition has not been found necessary. The material is prepared to be neutral or slightly alkaline. An excess of alkalinity is to be avoided.

Any inert gas such as air, carbon dioxide or nitrogen, the pressure of which can be carefully controlled to give a uniform flow, can be used in this determination.

The results obtained by the different analysts are not concordant. Some show excellent agreement, but the fluctuations on the whole

are too great. This may be explained by the fact that each of the collaborators introduced modifications of the method.

The results obtained by the associate referee and W. E. Stokes clearly indicate that this method can be applied successfully to the determination of fluorine in baking powder, with a recovery of approximately 90 per cent of the fluorine in the sample.

The following procedure is recommended for the preparation of a baking powder for the determination of fluorine:

Take 20 grams of baking powder in a porcelain evaporating dish. Place it in a muffle furnace at low heat and allow the volatile organic matter to burn off as completely as possible without allowing the furnace to come to the point where any redness is discernible, about 400°C. The resulting ash will be quite dark. Remove and allow to cool. Powder it again and add 10 cc. of a 50% solution of magnesium nitrate. (Be sure that the ash is thoroughly saturated without excess of the solution.) Drive off the excess of moisture in an oven and reheat in the muffle as before.

RECOMMENDATION.

It is recommended that the Wagner-Ross method as applied to the determination of fluorine in baking powder be submitted for further study.

DRUG SECTION.

REPORT ON DRUGS.

By G. W. HOOVER (Food and Drug Inspection Station, Transportation Building, Chicago, Ill.), *Referee*.

Your referee on drugs has no elaborate report to make. It may be stated that the work on the various subjects has been conducted by the associate referees according to the plan initiated several years ago. Some important investigations are completed with this year's report, and attention will be given to a few new subjects. It has been impossible to secure the assistance of as many associate referees as desired during the past year; however, considering the work as a whole, very satisfactory progress has been made. The associate referees deserve much credit for the excellent reports that will be presented on the various subjects at this meeting, and your referee is grateful to them and others who have manifested an interest by giving suggestions and assistance in the drug work for the association.

REPORT ON METHODS OF QUALITATIVE AND QUANTITATIVE ANALYSIS OF ARSPHENAMINE (SALVARSAN) AND NEOARSPHENAMINE (NEOSALVARSAN).

By G. W. Hoover and C. K. Glycart (U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.), *Associate Referees.*

The collaborative work on methods of analysis of arsphenamine and neoarsphenamine was continued this year in accordance with the recommendations approved by the association at the 1921 meeting[1].

Samples consisting of ampules of arsphenamine and neoarsphenamine of American manufacture and labeled with the serial numbers pertaining to the respective batches were forwarded to the collaborators. The directions submitted for the qualitative tests and the quantitative method, marked "Method No. 1", were substantially the same as adopted as tentative at the last meeting[2]. The directions for the quantitative method suggested by Engelhardt and Grantham, designated as "Method No. 2", were also submitted for study.

The following directions for conducting the work were sent to collaborators:

Qualitative tests for Arsphenamine (Salvarsan).

3,3′ —diamino—4,4′ —dihydroxy—arsenobenzene dihydrochloride corresponding to 31.57% arsenic.

$HCl.NH_2OH.C_6H_3.As : As.C_6H_3.OH.NH_2.HCl + 2H_2O.$

PHYSICAL PROPERTIES.

Arsphenamine is a pale yellow powder, unstable in moist air. It is soluble in water, 1 to 5 parts, methyl alcohol 1 to 3 parts, and only slightly soluble in ether. The aqueous solution is greenish yellow, and it reacts strongly acid to litmus. The moisture content is not more than 7.6% when dried in an atmosphere of hydrogen at 105°C.

CHEMICAL PROPERTIES.

An aqueous solution of arsphenamine (1 to 100) yields no precipitate with dilute mineral acids, with the exception of sulfuric acid (distinction from neoarsphenamine).

The addition of sodium hydroxide T. S. yields a precipitate which is soluble in excess of the reagent.

Heated with alkaline solution of potassium permanganate, ammonia is liberated.

Mayer's reagent produces a heavy orange-yellow precipitate.

Ferric chloride solution produces a brownish violet color, turning turbid.

Silver nitrate solution added drop by drop produces a dark red precipitate, changing to black.

Reinsch test is positive.

Hydrogen sulfide produces no precipitate even after addition of hydrochloric acid and warming.

---

[1] *J. Assoc. Official Agr. Chemists*, 1922, **5**: 529.
[2] *Ibid.*, 526.

Qualitative Tests for Neoarsphenamine (Neosalvarsan).

Sodium 3,3′ —diamino 4,4′ —dihydroxy—arseno-benzene-methylene—sulphoxylate.

$NH_2OH.C_6H_3.As : As.C_6H_3.OH.NH (CH_2O) OSNa.$

Mixed with inert inorganic salts.

PHYSICAL PROPERTIES.

Neoarsphenamine is a lemon-yellow powder, unstable in moist air, turning to a reddish brown color. It is readily soluble in water but only slightly soluble in alcohol or ether. The aqueous solution is neutral to litmus. On exposure to air the solution rapidly becomes dark brown.

CHEMICAL PROPERTIES.

A freshly prepared aqueous solution of neoarsphenamine (1 to 100) yields a tardy precipitate on addition of dilute mineral acids (distinction from arsphenamine).

The addition of 10% sodium hydroxide solution produces no precipitate (distinction from arsphenamine).

Solution of alkali carbonates produces no precipitate (distinction from arsphenamine).

Mayer's reagent produces no precipitate until the solution is acidified with dilute hydrochloric acid (distinction from arsphenamine, which yields a precipitate directly).

Ferric chloride solution produces a violet color, turning to dark red.

Silver nitrate solution produces a yellow color, quickly forming a black precipitate on heating.

If 5 cc. of dilute hydrochloric acid is added and the mixture heated, the irritating odor of sulfur dioxide will be evolved (distinction from arsphenamine).

METHOD No. 1.

Quantitative Determination of Arsenic in Arsphenamine and Neoarsphenamine.

REAGENTS.

(a) *3% hydrogen peroxide solution.*
(b) *Oxalic acid solution.*—Dissolve 1 gram in 100 cc. of water.
(c) *C. P. potassium iodide.*
(d) *C. P. potassium permanganate (finely ground).*
(e) *Potassium permanganate solution.*—Dissolve 1 gram in 100 cc. of water.
(f) *0.1N sodium thiosulfate solution.*
(g) *Sulfuric acid solution.*—10% by volume.

DETERMINATION.

Mix 0.2 gram sample with 5 cc. of 10% sulfuric acid in a 500 cc. Erlenmeyer flask, fitted with a ground-glass stopper. (A blank is conducted, using the reagents under the same conditions, and the amount of 0.1N sodium thiosulfate consumed is deducted.) Add 1 gram of finely powdered potassium permanganate in small portions, mix thoroughly and allow to stand for 10 minutes. Add 10 cc. of concentrated sulfuric acid in 2 cc. portions. Shake thoroughly after each addition. Allow to digest 10 minutes, rotating the flask frequently during this period. Add 5 cc. of hydrogen peroxide solution, and continue adding this solution drop by drop until the brown precipitate disappears. To remove excess of peroxide, add 25 cc. of water, boil gently for 10 minutes and carefully add a few drops of a 1% solution of potassium permanganate until the

pink color is just permanent. To remove excess of permanganate, add a drop or two of oxalic acid solution. Dilute with 50 cc. of water. When the solution is cool, add 2 grams of potassium iodide, stopper flask tightly and let stand for 1 hour in a cool place. Titrate the liberated iodine with 0.1N sodium thiosulfate, omitting the use of starch indicator.

1 cc. of 0.1N sodium thiosulfate is equivalent to 0.00375 gram of arsenic.

The arsenic content of arsphenamine should not be below 30 or above 32%.

The arsenic content of neoarsphenamine should not be below 18 or above 20%.

METHOD No. 2.

(Applicable for assaying organically combined arsenic products.)

Proceed with the directions under "Determination", Method No. 1, using the same reagents but omitting the blank and including "add 2 grams of potassium iodide". Let the solution stand for 1 hour.

ADDITIONAL REAGENTS.

Sodium sulfite solution.—Dissolve 2 grams in 100 cc. of water.

Sodium hydroxide solution, (1 *to* 1).

C. P. sodium bicarbonate.

0.1N iodine solution.

DETERMINATION.

Add from a buret, avoiding excess, the sodium sulfite solution to decolorize the liberated iodine. Add sodium hydroxide solution until slightly alkaline to litmus paper and render slightly acid with concentrated hydrochloric acid. Place the flask in cold water until the solution is thoroughly cooled; add 5 grams of sodium bicarbonate and titrate with 0.1N iodine solution.

1 cc. of 0.1N iodine solution is equivalent to 0.00375 gram of arsenic.

The results shown in the table were reported by the following collaborators: H. Engelhardt and R. I. Grantham, Sharp and Dohme, Baltimore, Md.; G. W. Raiziss, University of Pennsylvania, Philadelphia, Pa.; C. G. Remsburg, U. S. Public Health Service, Hygienic Laboratory, Washington, D. C.; and C. K. Glycart.

Results of determination of arsenic in arsphenamine and neoarsphenamine.

COLLABORATOR	METHOD No. 1.		METHOD No. 2.	
	Arsphenamine Sample A-1	Neoarsphenamine Sample N-2	Arsphenamine Sample A-1	Neoarsphenamine Sample N-2
	per cent	*per cent*	*per cent*	*per cent*
H. Engelhardt	31.4	18.6	31.4	19.5
R. I. Grantham	33.0	19.5	31.2	19.4
G. W. Raiziss	31.19	18.68	31.28	18.48
C. G. Remsburg	31.31	18.99	30.47	18.47
	31.41	19.07	30.56	18.47
				18.56
C. K. Glycart	31.21	19.28	30.38	19.23
	31.38	19.18	30.56	18.85

It appears that Method No. 1 has been considered generally satisfactory for the purpose of estimating the arsenic content of arsphena

mine and neoarsphenamine. Method No. 2 yields equally good results, as shown by comparison of the reports. Since it is based on the direct titration of the active constituent, that is, the arsenious acid, and no blank is required, this method should be given further consideration.

COMMENTS BY COLLABORATORS.

G. W. Raiziss.—It is our impression, however, that the method of Drs. Engelhardt and Grantham requires more work than the original method.

H. Engelhardt.—The results obtained by Method No. 1 are not as concordant as could be desired, but this is due to a varying blank test as already pointed out in our letter of May 12, 1921.

RECOMMENDATIONS.

It is recommended—

(1) That the qualitative tests and the quantitative method, No. 1, submitted for the examination of arsphenamine and neoarsphenamine be adopted as official methods.

(2) That the quantitative method, designated "Method No. 2" be adopted as a tentative method with the view to further study for final adoption.

(3) That during the next year the associate referee study and devise methods to determine the ratio of arsenic to nitrogen in arsphenamine and neoarsphenamine.

No report on the determination of alcohol in drug preparations was made by the associate referee.

No report on the determination of chloroform in drug preparations was made by the associate referee.

No report on analytical methods for the determination of silver in silver proteinates was made by the associate referee.

No report on the determination of camphor in pills and tablets by the alcohol distillation method was made by the associate referee.

No report on the distillation method for the estimation of santalol in santal oil was made by the associate referee.

REPORT ON TURPENTINE.

By J. O. Clarke[1] (U. S. Food and Drug Inspection Station, Savannah, Ga.), *Associate Referee.*

A study of two methods of polymerization begun last year was continued. Samples were sent to several collaborators, but no reports were received. The samples were pure gum turpentine containing known amounts of kerosene, as shown in the table.

The fuming sulfuric acid[2] and the sulfuric-nitric acid[3] methods were used on all the samples.

Results of polymerization of pure turpentine with known amounts of mineral oil.

SAMPLE	MINERAL OIL ADDED	FUMING SULFURIC ACID		SULFURIC-NITRIC ACID	
		Residue	Refractive Index 20°C.	Residue	Refractive Index 20°C.
	per cent	*per cent*		*per cent*	
A	0	1.2	1.5015	0	—
		1.2	1.5010	0	—
B*	0.5	2.0	1.4847	0.5	1.4477
		1.6	1.4853	0.2	1.4377
C*	1.0	2.4	1.4713	0.8	1.4395
		2.4	1.4716	0.9	1.4357
D*	2.0	3.2	1.4869	1 4	1.4496
		3.2	1.4829	1.0	1.4389
E	2.5	3.2	1.4720	1.8	1.4345
		3.2	1.4666	1.9	1.4356
F	5.0	5.6	1.4587	4.0	1.4354
		5.6	1.4562	4.1	1.4347

*Determinations by L. A. Salinger, U. S. Food and Drug Inspection Station, Savannah, Ga.

Both methods appear to give good results. Neither can be considered as strictly quantitative for the determination of mineral oil, but either gives an approximation of the amount present. When the amount of residue is considered in connection with its refractive index either method can be relied on to detect comparatively small amounts of mineral oil. On the particular sample of turpentine used in this work as little as 0.5 per cent was easily detected.

RECOMMENDATIONS.

It is recommended—

(1) That the fuming sulfuric acid method be adopted as tentative in the following slightly modified form:

---

[1] Presented by W. L. Heath.
[2] *Assoc. Official Agr. Chemists, Methods*, 1920, 306.
[3] *J. Assoc. Official Agr. Chemists*, 1922, 5: 552.

POLYMERIZATION.—TENTATIVE.

REAGENTS.

Fuming sulfuric acid.—Mix about 140 grams of concentrated sulfuric acid with sufficient liquid, fuming sulfuric acid (about 100 grams), to obtain an acid containing slightly more than 83.38 per cent of sulfur trioxide. Determine the exact strength of this mixture and also of the concentrated acid as follows: Weigh out a suitable amount of acid in a bulb, having a capillary tube in the lower end and a tube with a stop-cock in the upper end, fitted with a platinum wire for suspending on a balance. (The bulb is filled with the aid of a slight vacuum, and the lower end of the capillary is emptied by closing the stop-cock simultaneously with the withdrawal of the capillary from the acid, after which it is wiped off, first with a wet and then with a dry piece of cloth.) Run the acid into cold water, make up to volume and titrate an aliquot of the solution against standard alkali. Calculate the sulfur trioxide content of the acid and add sufficient concentrated sulfuric acid to make it exactly 82.38 per cent of sulfur trioxide. The acid must be carefully protected against absorption of water from the air.

Concentrated sulfuric acid.—Specific gravity 1.84.

DETERMINATION.

Place 20 cc. of the sulfuric acid in a graduated, narrow-necked, Babcock flask; stopper, place in ice water and cool. Add slowly 5 cc. of the turpentine. Mix the contents gradually, cool from time to time and do not allow the temperature to rise above 60°C. When the mixture no longer warms on shaking, agitate thoroughly, place in a water bath and heat to 60–65°C. for about 10 minutes, keeping the contents of the flask thoroughly mixed by vigorous shaking 5 or 6 times. Cool to room temperature and fill the flask with concentrated sulfuric acid until the unpolymerized oil rises into the graduated neck. Centrifuge 4–5 minutes at about 1200 revolutions per minute, or allow to stand for 12 hours. Read the unpolymerized residue, notice its consistency and color and determine its refractive index.

(2) That the sulfuric-nitric acid method in the form published in *The Journal* be adopted as tentative.

(3) That the method of Grotlisch and Smith[1] for the determination of coal tar oils in turpentine be studied.

A NEW SEDIMENTATION TUBE AND ITS USE IN DETERMINING THE CLEANLINESS OF DRUGS AND SPICES.

By ARNO VIEHOEVER (Bureau of Chemistry, Washington, D. C.), *Associate Referee on Crude Drugs.*

The cleanliness of crude drugs is a question closely related to volume weight determination, as discussed in previous reports of the Associate Referee on Medicinal Plants[2].

The work of 1922 followed along the line of obtaining an easy and rapid method of determining the cleanliness of crude drugs. In the

[1] *J. Ind. Eng. Chem.*, 1921, 13: 791.
[2] *J. Assoc. Official Agr. Chemists*, 1920, 4: 149; 1921, 4: 409; 1921, 5: 155; 1922, 5: 553.

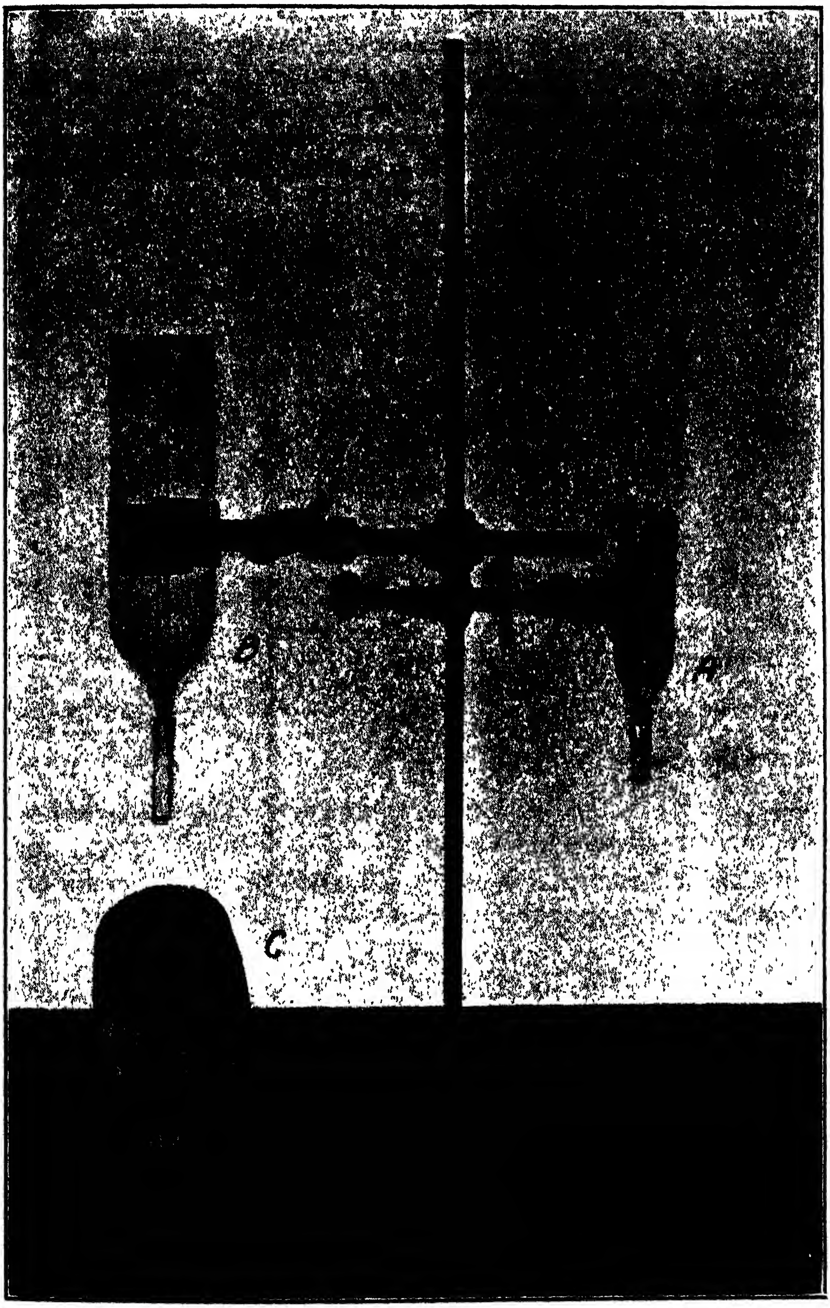


FIG. 1.—SEDIMENTATION TUBE.

A—Small tube containing approximately 30 cc. B—Tube containing approximately 200 cc. C—Support for centrifuging.

determination of total and acid-insoluble ash the attempt was made to ascertain the amount of foreign inorganic matter (dirt, sand, etc.) present. It was felt that a simpler method might be devised, by which the amount of inorganic matter could be determined. In a publication, entitled "Acid-Insoluble Ash Standards for Crude Drugs"[1], attention was called to the work on pennyroyal and the separation of excessive

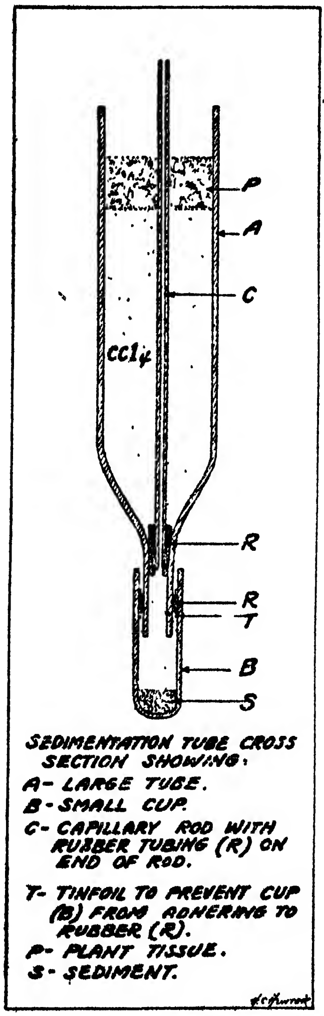


FIG. 2.—SKETCH ILLUSTRATING SEDIMENTATION TUBE.

A—Large tube. B—Small cup. C—Capillary rod with rubber tubing (R) on end of rod. T—Tinfoil to prevent cup (B) from adhering to rubber (R). P—Plant tissue. S—Sediment.

---

[1] Ewing, C. O., and Viehoever, Arno. Acid-Insoluble Standards for Crude Drugs. *J. Am. Pharm Assoc.*, 1919, 8: 725.

sand by means of carbon tetrachloride. The amount of sand found, as acid-insoluble ash, was 27.9 per cent, while a similar amount, 26.7 per cent, was obtained by separation with carbon tetrachloride.

Carbon tetrachloride has a specific gravity of 1.6, and, as far as the writer's experiments have gone, it appears to separate the plant tissue from adhering inorganic matter quite satisfactorily. Should generally useful results be obtained by the separation method, the work of ascertaining the degree of purity of a given drug would be greatly facilitated.

After preliminary experiments with various apparatus, the tubes A and B, illustrated in Fig. 1, were used.

PROCEDURE.

After the sedimentation tube (Fig. 2) is assembled, with the glass rod (C) removed, place the finely powdered drug—or the whole material, if of uniform size—in a tube containing sufficient carbon tetrachloride to permit floating and stir vigorously, so that the plant material will come in close contact with the liquid. The settling of the impurities can be effected either by means of the centrifuge or by setting the tube aside for 1 to 2 hours. Carefully insert the rod (C), with the rubber tubing (R) on the end, in the base of the large tube (A). This will permit the removal of the small cup (B), which contains the sand and dirt, without disturbing the contents in the tube (A). Decant the liquid from the residue and dry in the small cup (B) to constant weight at 100°C.

The size of the tube depends, of course, on the nature and amount of the material to be examined. In the examination of crude drugs and spices one or two grams are used with the small tube (A, Fig. 1), which holds about 30 cc. For larger amounts of solid material or liquids containing sediments[1] a larger tube, such as is illustrated by B (Fig. 1), holding about 200 cc., will prove satisfactory. A support (C, Fig. 1), devised by H. A. Lepper of the Bureau of Chemistry, will be found helpful in holding the cup in the centrifuge apparatus. Thus the cup is fixed firmly in place, both by a tin-foil-covered rubber band and by a rubber stopper fitted in the center of the wooden block.

WORK OF COLLABORATORS.

The efficiency of the sedimentation tube is proved by the results obtained, as given in Table 1.

The results show that checks can readily be obtained.

In order to establish the usefulness of the apparatus in the examination of crude drugs and spices, the following experiments were made:

WHOLE DRUGS (SPICES).

Whole cumin, found by J. F. Clevenger, Bureau of Chemistry, to yield, upon ashing, 8.4 per cent total ash and 1.1 per cent acid-insoluble

[1] Tankard, *Brit. Food J.*, 1922, **24**: 51, suggests the use of a similar apparatus with ground joints, to determine the sediment in milk. This apparatus can not be centrifuged.

ash, was shaken with carbon tetrachloride. The residue of 4 grams of fruits amounted to 0.035 gram and 0.038 gram, respectively, or 0.91 per cent residue as an average. It consisted mainly of small pebbles and dirt, the presence of which could thus be readily demonstrated.

TABLE 1.

Collaborative results showing efficiency of separation method.

COLLABORATOR	MATERIAL	AMOUNT OF RESIDUE	CHECK	ASH OF RESIDUE	CHECK
		per cent	*per cent*	*per cent*	*per cent*
H. A. Lepper, Bureau of Chemistry, Washington, D. C.	Tea	0.41	0.40	0.18	0.18
		0.45	0.44	0.21	0.20
		0.56	0.52	0.26	0.26
		0.54	0.60	0.33	0.31
		0.33	0.34	0.13	0.13
		0.26	0.30	0.14	0.13
		0.32	0.27	0.15	0.14
		0.30	0.28	0.12	0.12
		0.50	0.49	0.31	0.33
		0.28	0.29	0.17	0.16
		0.28	0.28	0.16	0.16
		0.18	0.19	0.09	0.10
		0.30	0.29	0.17	0.18
		0.34	0.33	0.13	0.13
		0.19	0.22	0.12	0.12
		0.45	0.41	0.27	0.27
		0.54	0.58	0.29	0.32
		0.39	0.36	0.22	0.20
		0.26	0.28	0.12	0.13
		0.25	0.26	0.16	0.14
Ruth G. Capen, Bureau of Chemistry, Washington, D. C.	Veratrum	7.3	7.3	....	....
		3.4	3.2	....	....
	Veratrum, rhizome	1.9	1.8	....	....
		2.8	2.8	....	....
	Veratrum, roots	3.1	3.6	....	....
		11.9	9.4	....	....
	Hydrastis	6.7	6.8	....	....
		2.4	2.4	....	....
	Geranium	4.5	4.5	....	....
	Aconite (mother)	1.1	1.3	....	....
	Menispermum	0.4	0.4	....	....
	Mandrake	0.3	0.2	....	....

POWDERED DRUGS.

Material, together with the small sedimentation tubes and a detailed outline of the procedure, with the suggestion to use 1 or 2 grams of material, was submitted to collaborators. It was suggested that the total and acid-insoluble ash of the material be determined according to the following outline:

Method for total ash.

Ignite 2 grams of the dry, ground drug, placed in a tared crucible and thoroughly moistened with alcohol, and incinerate the residue at a heat not to exceed dull red-

ness, to constant weight. If a carbon-free ash can not be obtained in this way, moisten the charred mass with alcohol. Allow the alcohol to burn off in the open and incinerate, repeating the alcohol treatment if necessary to obtain a white or nearly white ash.

Method for acid-insoluble ash.

Boil the ash obtained by the method for total ash with 25 cc. of 10% hydrochloric acid for 5 minutes. Collect the insoluble matter on a Gooch crucible or an ashless filter and wash with hot water, ignite at a heat not to exceed dull redness, and weigh.

The collaborative results are shown in Table 2.

TABLE 2.

Collaborative results on cleanliness of crude drugs and spices.

COLLABORATOR	PRODUCT	ASH		RESIDUE AFTER SEPARATION WITH CARBON TETRACHLORIDE	
		Total	Acid-insoluble	After standing	After centrifuging
		per cent	*per cent*	*per cent*	*per cent*
Ruth G. Capen.	Geranium	7.7	3.0	4.5	....
	Hydrastis	11.8	7.6	6.8	8.7
	Hydrastis	5.8	1.8	0.8	1.4
	Aconite (mother)	5.9	1.3	1.2	1.0
	Marjoram, fine powder	27.5	9.2	6.9	....
	Marjoram, coarse powder	11.3	2.7	2.0	....
	Menispermum	4.1	0.8	0.4	0.25
	Mandrake	3.2	1.2	0.4	0.5
	Veratrum, roots and rhizomes	13.0	9.0	7.3	10.4
	Veratrum, roots and rhizomes	19.0	15.0	17.0	....
	Veratrum, roots and rhizomes	12.0	8.0	7.3	11.5
	Veratrum, roots and rhizomes	6.1	3.6	2.8	3.6
	Veratrum, roots and rhizomes	16.5	12.7	10.5	16.1
	Veratrum, rhizomes	3.5	0.5	0.7	1.0
	Veratrum, rhizomes	3.6	1.2	1.2	1.5
	Veratrum, roots	6.6	3.2	4.2	4.5
	Veratrum, roots	9.2	3.7	3.4	4.5
J. J. McManus, Food & Drug Inspection Station, Savannah, Ga.	Aletris, No. 40 powder	15.50	12.57	17.57	....
		16.2	13.0	17.07*	....
	Hydrastis, powdered	10.26	5.3	2.3	....
		10.25	5.37	....	....
Geo. L. Keenan, Bureau of Chemistry, Washington, D. C.	Veratrum, fine	11.7	8.8	8.1	....
	Veratrum, coarse	4.2	0.9	1.1	....
	Hydrastis, fine	5.2	1.5	1.2	....
	Mandrake, coarse	3.2	0.3	0.9	....

*1 gram sample.

COMMENTS OF COLLABORATORS.

R. G. Capen.—The acid-insoluble ash in general is higher than the percentage of residue obtained on standing after separation with carbon tetrachloride.

The residue obtained after centrifuging in general is somewhat greater than that obtained after standing.

It is believed that this method furnishes a rapid means of obtaining an approximate result.

It has been found from experience that the fineness of the powder influences the amount of the residue obtained. The finer the powder, the more accurate the results, inasmuch as the separation of plant tissue and dirt is more complete.

J. J. McManus.—In regard to the method for separating dirt by the use of carbon tetrachloride, you will note that in the case of aletris results will be somewhat misleading. It must be that, in this drug, the dirt is so finely imbedded in the tissues of the plant that it will not separate and settle. The ash figure in the sediment indicates that not only does some of the dirt remain in the floating pieces of the tissue, but that part of the dirt brings down with it considerable organic matter. In this sample of aletris, which was ground to a No. 40 powder to obtain a better mixture, comparatively good checks were obtained on duplicate samples. In the separation method it was found easier to manipulate a one-gram sample of aletris as the amount of dirt separated from the two-gram sample more than filled the little tube.

In the one determination made on a sample of powdered hydrastis, the results were not very satisfactory, but it might be that after becoming more familiar with manipulating this method, better separation of the dirt could be obtained. The few experiments made with chenopodium are not listed. They indicated that the separation of dirt from these small seeds was not so rapid as one would ordinarily expect, and subsequent treatment of the floated matter would bring down more dirt and also some organic matter. * * * It was also noted that the residue in the small tube must be allowed to dry very slowly to prevent sputtering. It does not seem from the very few data which I have on hand, that the method is sufficiently accurate for general use. It does seem that it might have possibilities for use in the trade for easily determining the amounts of dirt in a small number of drugs which are handled continuously. For instance, a handler of anise or caraway might take a measured amount and quickly shake it in one of the tubes and allow it to stand for a set period of time and note the height of the sediment in the tube of standard diameter, and by comparing the results on the new samples with the results on samples known to pass the standard, could easily get an idea of the approximate excess of dirt in his sample. The comment on this would probably be that a tradesman handling continuously a certain line of drugs would become so familiar with their physical appearance that he could note the dirt without using this method. However, the method does seem to be a very interesting one, and I would like to do some more work on it.

Geo. L. Keenan.—The carbon tetrachloride separation method appeared to give satisfaction for the purpose of separating dirt in powders, the finer the powdered crude drug, apparently, the more consistent the results obtained. As a rough working method for the determination of the amount of dirt present in a crude drug which has been finely ground, it appears from the work done thus far that such a method might be desirable.

SUMMARY.

(1) Further work should be done to establish more definitely certain facts, *e. g.*, the influence of fineness of powder in various types of material upon the final result and the composition of the dirt, separable as residue in carbon tetrachloride, by standing as well as by centrifuging.

(2) The separation method, by means of tetrachloride, is recommended as a rapid procedure to obtain a definite indication of the degree of purity.

(3) The sedimentation tube described should prove to be a valuable apparatus, capable of wide application, since it permits of centrifuging and ready separation of the sediment.

SUBLIMATION OF PLANT AND ANIMAL PRODUCTS—THIRD REPORT.

By ARNO VIEHOEVER[1] (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*

The sublimation experiments reported at the 1920 and 1921 meetings[2] were continued.

Various apparatus were tried out—those that permit the sublimation of small quantities only, about 0.1 gram of material (microsublimation), and those in which both minute as well as larger amounts may be sublimed. Figure 1, A to D, shows various types used in the work. Figure 1, A, represents practically the apparatus of Eder[3], with the difference that it provides for cooling. It is described in greater detail in the discussion of the collaborative work. Figure 1, B, shows an apparatus of simpler form, in which the ground joints are eliminated, thus permitting of easy construction in any laboratory. A very simple apparatus illustrated by Fig. 1, C, represents an Erlenmeyer suction flask in which a test tube, filled with water, is introduced. It is possible, of course, to provide for the circulation of water, as shown in the other apparatus.

A specially constructed sublimation flask, devised by the writer, is shown in Fig. 1, D. This apparatus, as well as various modifications shown in the sketches (Fig. 2), has proved very satisfactory. The flask should be made of Pyrex or Jena glass, in order to withstand marked differences in temperature to which the flask, especially the constricted area, is subjected during the experiments. It can be made by a glassblower at small cost. It permits of the ready sublimation of quantities of material within the general range needed in analytical work.

The lower bulb-like part of the apparatus is heated in a suitable bath. At present cottonseed oil is used, since it has been found very satisfactory at temperatures up to 225°C. and over. The oil is placed in a metal crucible. Uniform heat is supplied by an electrically heated shell[4], which is preferred to an open flame. This shell is prepared from long-fibered asbestos and plaster of Paris, moulded around the crucible and wired; it gives a wide range of heat. Figure 1, F, shows this heater with rheostat. The available means to provide heat, *e. g.*, gas, or another bath (sulfuric acid, glycerin or sand), can also be used instead of the one suggested. The flask is inserted into the bath to approximately the middle of the constricted neck.

---

[1] Presented by J. F. Clevenger.
[2] *J. Assoc. Official Agr. Chemists*, 1921, 4: 414; 1922, 5: 557.
[3] Eder, Robert. Über die Mikrosublimation von Alkaloiden im luftverdünnten Raum, *Schweiz. Wochschr.*, 1913, 51: 228, 241, 253.
[4] Constructed by J. F. Clevenger, Bureau of Chemistry, Washington, D. C.

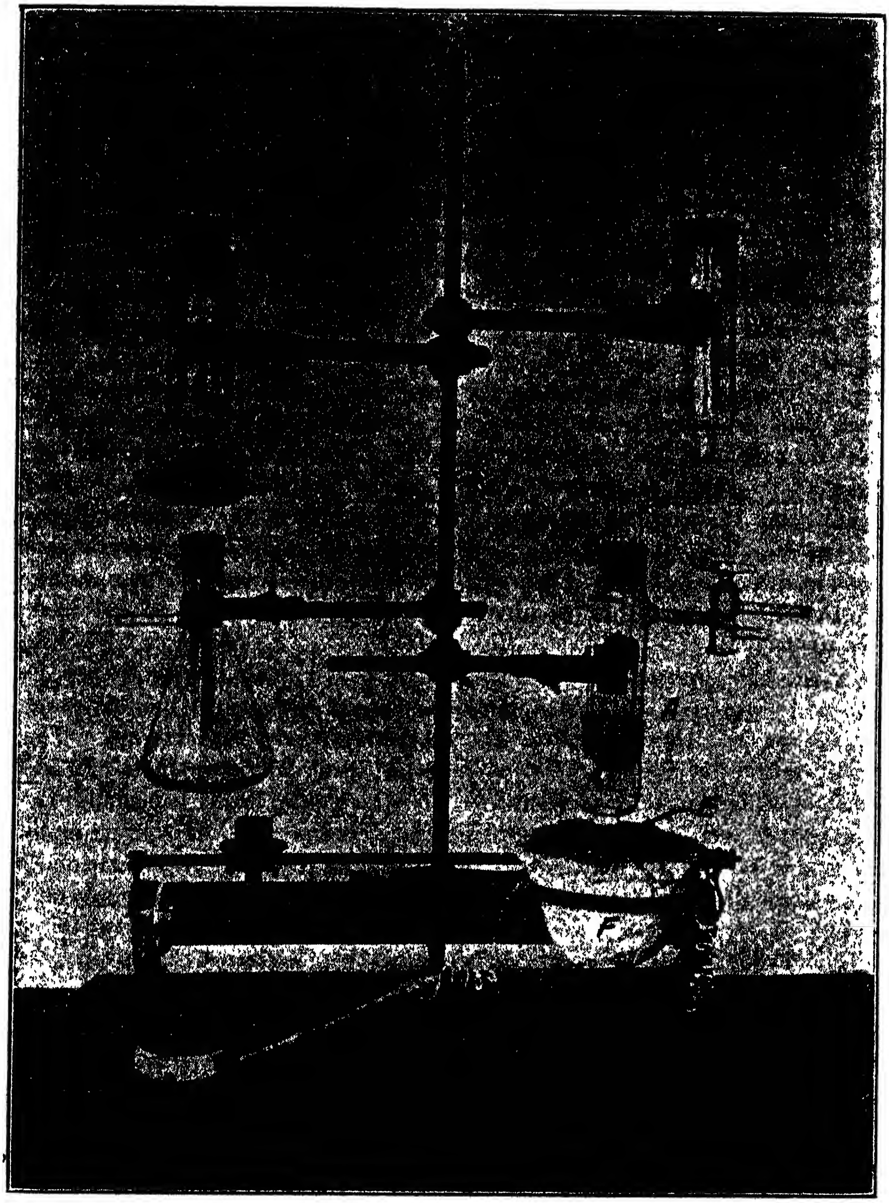


FIG. 1.—SUBLIMATION APPARATUS.

A, B—Microsublimation apparatus adapted to vacuum and cooling. C—Suction flask adapted to sublimation. D—Sublimation flask for micro- and macrosublimation. E—Oil bath (cottonseed). F—Heating shell.

Sketches 1 and 2 (Fig. 2) provide for outside cooling by means of either a waterjacket or a copper coil with running water, and Sketch

3 provides for inside cooling. The distinct ridge in the upper neck end, visible in all the sketches, together with the downward curved bottom of the inner condenser, Sketch 3, prevents such liquid-condensation products as water, fat, etc., which may be formed during the heating, from dropping back into the original material.

The ridge may be covered with a cover-glass, to receive small amounts of sublimate for microscopic examination, or with a porous diaphragm (platinum gauze), or a perforated disk (3/8 inch in diameter), which prevents the dropping back of the sublimate to the original material.

The neck-like constriction permits of the insertion of a stopper. Sketch 3 (Fig. 2), shows the inner walls of the neck, ground to make a good joint, with a glass stopper at the end of the glass rod, introduced after sublimation. A rubber stopper fastened to a rod will usually do as well, especially if protected from the ready attack of organic solvents by tin-foil. This stopper separates the sublimate from the original material. Thus, the cylindrical part of the apparatus, containing part or the whole of the sublimate, can be readily washed out with liquids suitable to dissolve and remove this sublimate. A small notch in the wall of the opening will, of course, facilitate this removal.

The following approximate dimensions may assist in the construction of a suitable apparatus.

PARTS	DIAMETER	HEIGHT	APPROXIMATE CAPACITY
Sublimation flask	....	......	150 cc.
Bulb	6.3 cm. (greatest)	3.8 cm.	62 cc.
Constriction	1.9 cm.	1.6 cm.	2-3 cc.
Cylinder	4.2 cm. (outer)	9.5 cm.	85 cc.
	3.8 cm. (inner)	......	......

COLLABORATIVE WORK.

The collaborative work was carried out by Ruth G. Capen, Bureau of Chemistry, Washington, D. C.; P. B. Clark, Food and Drug Inspection Station, San Francisco, Calif.; and C. K. Glycart, Food and Drug Inspection Station, Chicago, Ill. Joseph F. Clevenger collaborated in the improvement of the apparatus. Samples of *Mylabris* (Chinese flies), containing cantharidin; *Artemisia cina* (wormseed), containing santonin; and *Ilex cassine* (Cassine), containing caffeine, were submitted to these workers, together with one apparatus for the sublimation of small quantities of material, and another for the observation of the melting and subliming points of crystals under the microscope.

MICROSUBLIMATION APPARATUS.

This apparatus (Fig. 1, A) is adapted to qualitative sublimation of plant products. It consists primarily of two pieces fitted together with a ground joint. The smaller piece has a narrowed extension in which the material to be sublimed is placed. On the shoulders of this piece

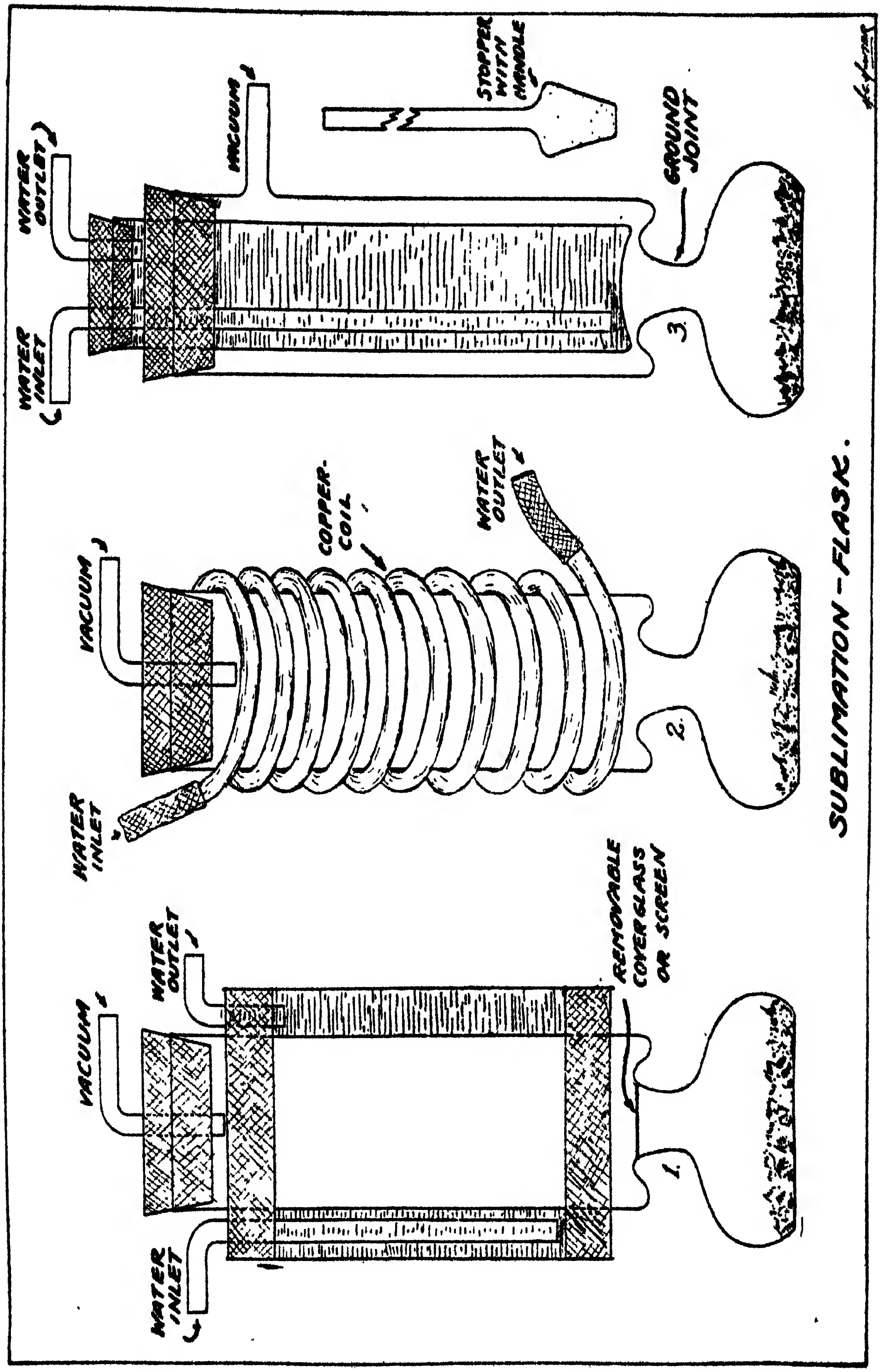


FIG. 2.—MODIFICATIONS FOR OUTSIDE AND INSIDE COOLING.

a round cover-slip, approximately 18 mm. in diameter, is placed to receive the sublimate. The larger piece is provided with a tube having a three-way stop-cock through which a vacuum is applied. The upper portion is provided with an opening through which a water-cooling device may be introduced.

PROCEDURE.

After assembling, heat the substance in the apparatus by immersing the narrow extension of the smaller piece into a heated bath of cottonseed oil. A medium flame is used for sublimation, and the temperature is usually not increased beyond 10°C. of the melting point of the substance to be sublimed. The temperature is determined by placing the bulb of the thermometer directly in the oil bath. The time of heating varies from less than one hour to several hours, depending upon the ease of sublimation—the higher the vacuum the more effective the sublimation.

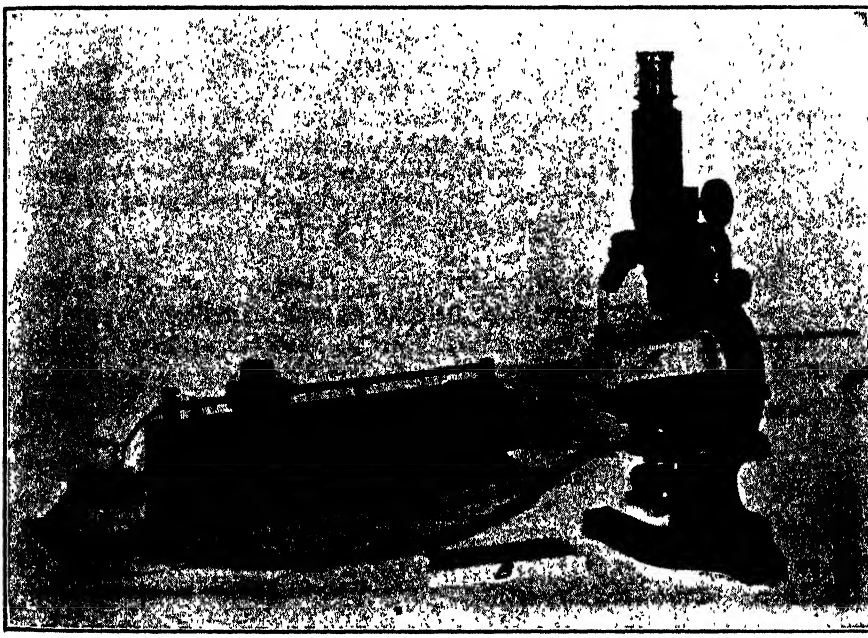


FIG. 3.—MICROMELTING-POINT APPARATUS.

A—Heating block carrying object slide. B—Cover enclosing slide in heating chamber. C—Rheostat for temperature control.

MICROMELTING-POINT APPARATUS.

This apparatus is adapted for the observation, under the microscope, of the melting point or temperature of sublimation of crystalline substances. It was devised by B. J. Howard of the Microchemical Laboratory, Bureau of Chemistry, and consists of the following parts:

The lower section, consisting of a block of metal with a triangular extension, is modified to take care of the object slide. The extension is heated by means of an

alcohol or gas flame. On the end opposite the extension a hole is provided for the insertion of a thermometer. Another hole in the middle of the block permits observation of the object by transmitted light. An upper section, serving mainly as a cover, fits tightly over the lower part of the block. The outer surfaces of the apparatus, with the exception of the triangular extension which is to be heated, are covered with asbestos board glued to the metal surface with sodium silicate. The apparatus is placed upon the stage of the microscope, and observations are made directly, while the apparatus is being heated.

An improvement of this apparatus by Clevenger[1] provides for heating with electricity (Fig. 3). By this means better control and temperatures as high as 400°C., and over, are obtained.

PROCEDURE.

The melting point can usually be determined by observing the temperature at which the crystals lose the ability to polarize light. Thus far the simple apparatus has readily permitted the observation of melting points up to 200°C., or slightly over.

The sublimate heated in the melting-point apparatus may partially sublime on the small cover-slip located in the upper portion of the apparatus. The sublimation point is not sharply outlined. It represents the temperatures at which the crystals become visibly smaller through sublimation and finally disappear. The heating of the substance in narrow capillary tubes placed in the apparatus under the microscope, will, as J. F. Clevenger has shown in the case of cantharidin, retard sublimation, and thus permit the observation of the melting point.

The important factors in sublimation are temperature of the bath, air pressure, time of heating and melting, as well as subliming points of the substance under examination. For the identification of crystals obtained it is desirable, in addition to the properties enumerated above, to determine as many optical and chemical reactions as possible.

REMARKS SUBMITTED IN CONNECTION WITH PROCEDURE.

Caffeine.—Characteristic crystals are obtained by treating the sublimate with aqueous chloral hydrate solution (5+3), or mercuric bichloride solution (0.1 per cent).

Cantharidin.—If the insect material is moistened with hydrochloric acid alcohol (1+9) before it is heated, larger amounts of cantharidin are obtained. Characteristic crystals are secured by treating the sublimate thus obtained with barium hydroxide solution (about 5 per cent).

Santonin.—The sublimate is usually deposited on the cover-glass in droplets, which, upon standing, especially at a temperature of about 100°C., develop into large crystals. The formation of crystals may be hastened by treating the sublimate with ether.

The following results were obtained:

[1] The detailed construction will be discussed in a subsequent publication.

Sublimation of plant and animal products.

MATERIAL USED	TEMPERATURE OF BATH	AIR PRESSURE	TIME OF HEATING	MELTING POINT	SUBLIMATION POINT	CRYSTAL FORM	SUBSTANCE OBTAINED
	°C.		*hours*	°C.	°C.		
Ilex vomitoria (Ait.)	130–140	100–3mm.	½–1	......	135‡	Needles	Caffeine*
	130–150	Normal atmospheric	¼	......	133	Needles	Caffeine†
Mylabris cichorii§ (Fab.)	110–120	760–3mm.	¼	......	100–110‡	Plates	Cantharidin*
	120	Normal atmospheric	½	......	109	Plates	Cantharidin†
Artemisia cina(Berg.)	135–170	20–3mm.	½–1	165–170	155–160‡	Plates and needles	Santonin*
	170	Reduced pressure**	1	168	173	Close plates	Santonin†

*Determinations made by R. G. Capen.
†Determinations made by C. K. Glycart.
‡Determined from resublimation of crystals at normal air pressure obtained with the micromelting-point apparatus.
§Treated with hydrochloric acid.
**Not determined. No manometer available.

COMMENTS OF COLLABORATORS.

P. B. Clark.—A number of difficulties were encountered in the use of the microsublimation apparatus so a little different form of apparatus was devised (Fig. 4). The sample of wormseed was the only one used, but several things were noted in trying to obtain a crystalline sublimate which would also apply to a number of other drugs. In the first trial the time, temperature and pressure given in Dr. Viehoever's letter was used, and it was found that a large quantity of oil (probably both volatile and fixed) was deposited on the cover-slip with the santonin, and the santonin failed to crystallize. The apparatus was then charged with a fresh sample of santonica, a 6-inch vacuum maintained and a fresh cover-slip was placed in the apparatus for every 10° rise in temperature, starting with 90°C., each cover-slip being held in the apparatus about 45 minutes. No crystals were obtained until a temperature of 150° to 160° was reached, although all but the first two cover-slips gave a positive test for santonin. This experiment was repeated several times, the temperature being raised as high as 200°C., and chemical tests showed that santonin was still being sublimed at 200°C.

In the light of the foregoing experiment it does not seem as though this method would be very reliable for determining melting points, as the purity of the sublimate would be doubtful owing to the presence of fixed and volatile oils and the probability of some destructive distillation taking place. The sublimate on the cover-slip might, however, be used for making short tests for active principles in drugs where absolute purity would not be necessary to make a test.

C. K. Glycart.—The qualitative tests performed according to directions were entirely satisfactory with the following reagents:

Caffeine	Mercuric chloride	Fine needles
Cantharidin	Barium hydroxide solution	Large and small crystals
Santonin	Furfural-sulfuric acid	Purple, changing to dark opaque solution

The hydriodic acid test was not performed as this acid was not available. The droplets of cantharidin required time to crystallize.

The determinations are easily performed by use of the apparatus supplied, and the methods should prove to be of great value.

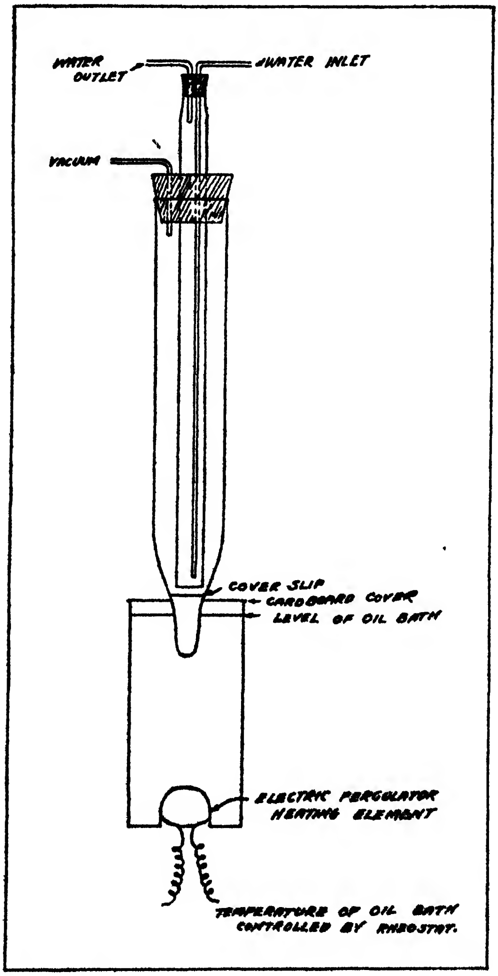


FIG. 4.—MICROSUBLIMATION APPARATUS (AFTER CLARK).

SUMMARY.

The experimental work on the improvement of sublimation apparatus led to the construction of a sublimation flask. This is an inexpensive apparatus, which permits of the sublimation of minute as well as fair-sized quantities of material.

The task of definitely identifying the sublimate resulted in a notable improvement of an apparatus permitting the observation of the melting and subliming points under the microscope.

The collaborative work has produced valuable suggestions in the improvement of the apparatus and has demonstrated the fact that sublimation carried out by various workers under like conditions will yield like results.

RECOMMENDATIONS.

It is recommended—

(1) That the work on the sublimation of plant and animal products, as well as any other materials representing or yielding sublimable constituents, be continued.

(2) That in this work the improved apparatus, or any other apparatus or modifications available in the course of the work, be used.

(3) That the methods for the isolation and identification of cantharidin, caffeine and santonin be adopted as tentative methods.

SUBLIMATION AS AN ANALYTICAL PROCEDURE.

By Julius Hortvet (State Dairy and Food Commission, St. Paul, Minn.).

On the subject of sublimation as commonly practised in the laboratory, Gorup-Besanez[1] commented in 1855 as follows: "The sublimation of organic bodies is an operation which must often be used for their purification. In such cases the amount of material at hand is limited, and the losses entailed by recrystallisation, decolorisation and similar operations are so considerable that it seems very desirable to reduce these losses to a minimum in order that the thorough examination of such bodies may be facilitated".

The process of sublimation has, in recent years, found increased serviceability as a laboratory operation. Though not frequently applicable in the analysis of inorganic substances, the process has been found to be of considerable importance in the examination of a large number of organic compounds and mixtures. Approximately 150 sublimable substances—20 inorganic and 130 organic—are listed in Olsen's Manual (1922). There are also many compounds not included in the Manual that are known to be susceptible to sublimation under modified conditions.

[1] *Ann.*, 1855, 93: 265.

GENERAL AND QUALITATIVE.

Sublimation is often very serviceable in the separation and purification of substances. As well-known illustrations may be given: the separation of pyrogallic acid, benzoic acid, oxalic acid, salicylic acid, vanillin, etc., from crude material or impurities; the separation of strychnine, morphine, cocaine, santonin, and other active principles from crude drugs; the separation of caffeine from coffee and tea, gentisin from gentian root, and cantharidin from the dried insect, cantharides. Pure oxalic acid and benzoic acid are readily prepared in a high state of purity by sublimation for use in making standard solutions. By means of sublimation a distinction can often be made between genuine tea leaves and tea substitutes, between genuine Levant wormseed and the domestic variety, and also in many instances between standard and exhausted drugs.

The method is serviceable in many cases for the purpose of affording an indication regarding the best course to be pursued in a chemical analysis, and it may also serve as a useful sorting-out test in the preliminary examination of a great variety of substances. It has been shown[1] that a large number of alkaloids which formerly were not found to be sublimable under ordinary conditions are, on the other hand, rendered sublimable in vacuum, as for example, hyoscyamin, papaverine and narcotine. In the case of such alkaloids as strychnine, morphine and cinchonine beautiful crystalline sublimates are obtained. By means of rapid sublimation under vacuum, definite crystalline deposits are formed in the case of substances with high vapor pressure, as caffeine, theobromine and cantharidin. The crystal formations are constant and characteristic for definite alkaloids, although in some cases they exhibit unusual behavior. Cantharidin is readily separated from the male or female insect, or from the eggs, by moistening the finely divided material with strong hydrochloric acid, followed by sublimation, and evaporation of any condensed acid by exposing the sublimate over unslaked lime (Fig. 1).

In addition to their vesicating properties, melting-point and polarizing action upon light, the crystals may be identified by their behavior with baryta water.

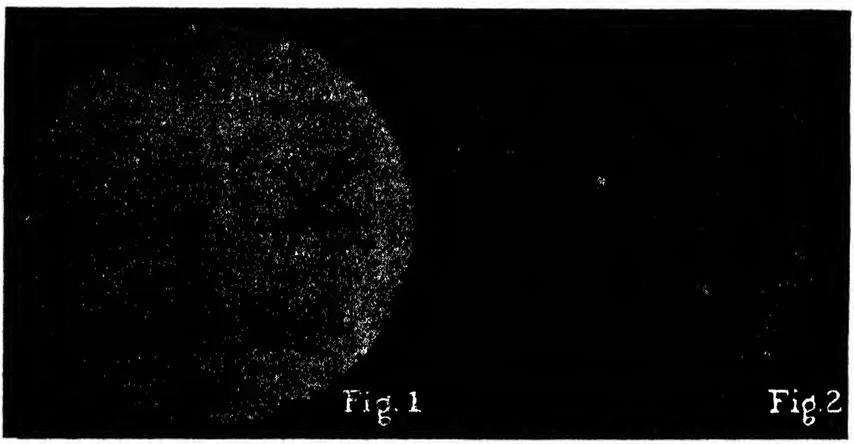
QUANTITATIVE APPLICATIONS.

A number of quantitative methods are improved and materially shortened by resorting to sublimation. In many instances the process may be applied directly to the properly prepared material; in other cases previous extraction, using a suitable solvent, may be resorted to, then the impure residue subjected to sublimation for the purpose of

[1] Eder R., *Schweiz. Wochschr.*, 1913, 51: 228, 241, 253.

obtaining the compound in a condition of greater purity. As illustrations may be given: the separation of benzoic acid, salicylic acid, saccharin, etc., from residues obtained by extracting food products with ether and other solvents. Sublimation applied to the residue after evaporating the chloroform from an extract obtained from catsup yielded 0.086 per cent benzoic acid, which, calculated to sodium benzoate, gave 1.101 per cent. The sample of catsup was represented on the label to contain 0.10 per cent of sodium benzoate. The modified Stahlschmidt method applied to a sample of ground coffee yielded 1.32 per cent caffeine. By direct sublimation of the same coffee, using a 1-gram sample, there was recovered 1.92 per cent caffeine plus impurities. The material was washed out from the sublimator by means of chloroform, the solvent evaporated, and the residue mixed with inert material (sand) and subjected to repeated sublimation, with the result that 1.26 per cent pure caffeine was obtained. This result was checked by means of the nitrogen determination according to official method[1]. Another sample of coffee subjected to the same procedure, but under changed conditions, yielded 1.39 per cent caffeine on first sublimation and on second sublimation, 1.35 per cent. A number of trials carried out on known mixtures of active material mixed with inert material (sand) yielded results as follows:

Santonin	0.100 gram, yielded 0.0988 gram.
Camphor	0.052 gram, yielded 0.0513 gram.
Benzoic acid	0.141 gram, yielded 0.1400 gram.



CANTHARIDIN ARSENIC TRIOXIDE.

The camphor sublimation was conducted under ordinary atmospheric pressure. The above are only a few preliminary trials. Investigations

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 270, par. 15.

are to be continued so as to cover a considerable variety of food products, pharmaceutical preparations and drugs.

MICROSUBLIMATION.

By means of a suitable apparatus, characteristic sublimates can be obtained from very small amounts of material. It is possible in many cases, for purposes of identification[1], to isolate from a complex mixture or from a crude drug, substances in definite crystalline form. Investigations have demonstrated the applicability of microsublimation in vacuum as a valuable analytical method and as a means of identifying poisonous plant-base forms, also its usefulness in connection with microchemical reactions as a valuable method in forensic chemistry. The microscopic appearance of a sublimate will frequently give valuable confirmatory evidence, or will suggest the course that should be followed in carrying out a systematic investigation of a substance submitted for analysis. The work of Eder[2] and others has demonstrated the advantage of carrying out sublimation tests under reduced atmospheric pressure and by means of carefully controlled methods of heating.

Among results obtained by Eder on various alkaloids sublimed under pressures ranging around 10 millimeters are the following:

Cocaine	between 75 and 90°	Chenine	between 130 and 148°
Atropine	between 100 and 130°	Narcotine	between 146 and 156°
Codeine	between 93 and 110°	Brucine	between 158 and 175°
Solanine	between 158 and 184°		

The following results were obtained in the laboratory of the Minnesota Dairy and Food Department on various substances sublimed under reduced pressures varying from 23 to 25 millimeters:

Initial Sublimation Temperatures.

Vanillin	53°	Menthol	41°
Benzoic acid	47°	Resorcine	65°
Caffeine	80°	Phenolphthalein	124°
Salicylic acid	64°	Santonin	127°
Oxalic acid	110°	Hexamethylene-tetramine	90°
Camphor	37°	Cantharidin	93°

Further practical applications of microsublimation were made with strychnine and arsenic. A sample of strychnine alkaloid weighing less than 0.001 gram was sublimed on a microscope slide, and characteristic crystalline deposits were obtained. Arsenic trioxide mixed with chopped meat in proportion approximating one part in 100,000 was subjected to the Reinsch test. The copper-foil was cut up into small pieces and packed into the narrow base of a glass capsule placed inside the sublimator, the capsule covered with a microscope slide, the apparatus

[1] Viehoever, Arno, *J. Assoc. Official Agr. Chemists.* 1921, 4: 414; 1922, 5: 557.
[2] *Schweiz. Wochschr.*, 1913, 51: 228, 241, 253.

connected with a vacuum pump and the heating conducted cautiously until a deposit was observed on the slide. On examining the deposit under the microscope characteristic octahedral crystals were identified. (Fig. 2.)

For the purpose of further verification the deposit was subjected to solubility tests with various reagents. A similar process may be applied to crude drugs or to vegetable powders to obtain sublimates in a condition exhibiting characteristic features of any volatile crystalline principle which they may contain. The appearance of a sublimate may, in certain instances, vary somewhat according to the rate of sublimation, amount of moisture and other factors. It may, however, be pointed out that it is possible, by means of a suitable contrivance, to remove moisture from the inside of the apparatus prior to adjusting temperature and vacuum conditions necessary for the sublimation. Having once obtained a sublimed deposit on a microscope slide great possibilities are available in the line of microchemical precipitates for the purpose of identifying various substances. In many instances the microscopic structure of a precipitate is a reliable method of distinguishing between two or more closely allied substances.

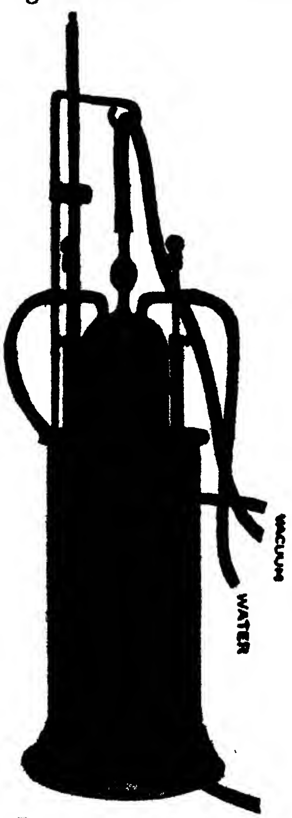


FIG. 3.—HORTVET SUBLIMATOR.

THE SUBLIMATOR.

In order to meet the requirements incidental to the various operations involved in sublimation processes, a new model sublimator has been designed to serve all the purposes which have been fulfilled, to a greater or less degree, by a number of well-known laboratory devices.

The construction of the sublimator involves the following features:

(1) *The sublimation cell*, consisting of an upper and a lower glass section tightly joined by means of accurately ground surfaces.

(2) *Sublimation chamber* (upper section), containing the cooling bulb placed centrally so as to receive the deposit of sublimed material.

(3) *The sublimation cup* (lower section) constructed for the purpose of holding various receptacles containing material to be subjected to sublimation.

(4) *A porous diaphragm*, fitted between the upper and lower section, serves—

(a) to allow the complete passage of the subliming material from the lower chamber into the upper, and

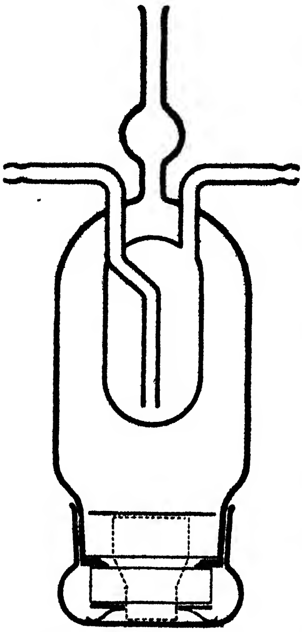


FIG. 4.—SUBLIMATION CELL.

(b) to prevent the sublimed material from falling back from the surface of the bulb into the cup.

For all general uses, a 100-mesh platinum gauze diaphragm is most satisfactory. A diaphragm of porous material other than platinum must be used in sublimation work with compounds destructive to platinum.

(5) *Glass dishes*, provided of various capacities and shapes suitable for different purposes. An adjustable spring support rests on the bottom of the cup and serves to fit the dishes in suitable position beneath the diaphragm. For microsublimation, a glass capsule with narrow base portion rests in a vertical position in the central hole of the spring support. A microscope slide placed in the upper section rests on the ground edge at the top of the capsule when the upper and lower sections are joined. After being removed from the subliming cell, the slide is placed in a specially constructed glass holder which fits on the microscope stage and thus permits examination in the usual manner.

(6) *The bulb tube*, sealed vertically at the top of the subliming cell serves for connection with the vacuum pump, thus permitting the adjustment of pressure to any degree desired. After disconnecting the rubber tubing from the upper section and detaching the base section or cup, the subliming chamber is turned to an inverted position (without the removal of the diaphragm); the sublimed material is then removed by means of a suitable solvent and washed out through the bulb tube into a beaker or crystallizing dish.

(7) *The heater*, consisting of an adjustable copper cup constructed in two sections so as to permit adjustment of depth. The cup is supported on a cylindrical sheet-metal stand at the base of which is placed a small gas burner. The depth of the heating cup is varied by lowering or raising the supporting rods which are riveted to the inner section. The adjustable cup serves the purpose of varying the temperature conditions to meet the requirements of the experiment in hand. A metal rod rests vertically on the upper surface of the heater and is provided with a clip for the purpose of supporting a thermometer to be used for temperature control. A loop at the upper end of the rod is for the purpose of holding the pressure-tubing which connects the bulb-tube at the top of the sublimator with the vacuum pump.

THE USE OF THE SUBLIMATOR.

The heating cup is placed on the sheet-metal support and rigidly secured in position by tightening the set-screws. A suitable heating bath is provided by means of a one-inch depth of clean, dry sand placed in the bottom of the cup. Care is taken that no sand grains are permitted to lodge in the space between the two cup sections and thus interfere with, or effectually prevent, the up-and-down movement of the inner section. The cup is adjusted to a depth of about three inches and set in position by means of the thumb-screws provided at the top of the posts.

The properly prepared and dried substance to be subjected to sublimation is mixed with a suitable amount of inert material—as pure ignited sand of about 40 mesh or powdered magnesia—the well-mixed material placed in one of the glass dishes suitable for the purpose and the dish placed in the subliming cup, resting centrally on the spring support. It is desirable that the dish be filled with material to near the top edge, thus bringing the surface of the contents close to the diaphragm. The diaphragm is placed in position on the glass projections, a thin film of vaseline or other suitable material is spread on the ground-glass surfaces of the upper and lower sections, and then by a firm though gentle pressure accompanied by a turning movement the two parts are tightly fitted together. When the spring support and dish are properly placed in the cup the top edge of the dish will be in close contact with the lower ground surfaces of the projections. The subliming cell is lowered into the heater and gently pressed down into the sand-bath so as to bring the sand well around the widened portion of the base, and the heater cup is lowered to its full depth. By means of rubber tubing the apparatus is connected with the water tap in such a manner as to afford a slow stream of cold water through the cooling bulb. The bulb-tube at the top is connected with the vacuum pump by means of pressure-tubing passed through the metal loop above. A vacuum gage (preferably a mercury manometer) is connected in position between the pump and the sublimator. When using a water pump, a trap is placed between the pressure gage and the pump, in order to prevent a sudden back-flow of water in the direction of the apparatus. For efficient heating in general sublimation operations, such as the purification of substances and quantitative separations, the cup is adjusted to its full depth, thus submerging the sublimation chamber to approximately two-thirds of its height. For microsublimations and for operations requiring the application of heat only to the base portion, the heater is adjusted to a shallow depth of about two and one-half inches. When all connections are properly made and tested and adjustments correctly arranged, the gas burner is placed

on the base beneath the heating cup and the flame adjusted to a small size, hardly exceeding one inch in height or even lower. Great caution should be exercised in the adjustment of the flame in order to prevent overheating or too rapid heating of the apparatus. The thermometer is supported in the clip and lowered until the bulb is fairly covered in the sand-bath.

The sublimation process is clearly observable with the aid of an electric light bulb placed near the apparatus, and a fair judgment is thereby obtained as to the progress of the experiment. When the material appears to be completely deposited on the condensing bulb, the pump is shut off, the vacuum carefully released, and the water inflow tube disconnected and closed by means of a rubber cap; the outflow tube is then disconnected and closed in the same manner. The flame is turned off, the cell removed from the heater, allowed time to cool, and the base portion detached. After the subliming chamber is turned to an inverted position, without removal of the diaphragm which falls loose into the space between the bulb and the outer shell, the deposit on the bulb is washed through the bulb-tube into a crystallizing dish by means of a suitable solvent (ether, chloroform, or other fluid). The dissolved sublimate may be passed through a funnel, or through a filter if deemed necessary in order to separate insoluble impurities. After evaporation of the solvent the dish and contents are placed in a desiccator for a short time and weighed. The weight of the sublimed deposit can also be obtained direct by draining the water from the bulb, removing the remaining traces of water by means of successive small portions of alcohol and ether followed by passage of a current of dry air, drying in a desiccator and weighing. The material may be subjected to further examination by separating a small portion from the condenser bulb or from the crystallizing dish and submitting it to the procedure described by Chamot[1]. Further purification of the material may be effected by repeating the sublimation in the manner described. The heating is conducted gradually, beginning at a low temperature, and controlled so as to diminish the impurities in the sublimate. For microsublimation where only a very small quantity of sublimable substance may be present, the material is placed in the narrow base portion of the subliming capsule supported in the circular opening at the center of the spring support. The specially made glass slide is inserted so as to rest on the projections at the base of the subliming chamber and the cup section connected, thereby resting the slide across the top of the capsule. The apparatus is then placed in the heating cup adjusted to a depth of about two and one-half inches. Connections with the water stream and vacuum pump are made in the

[1] Elementary Chemical Microscopy, 1916, 288–292.

usual manner, and the heating is conducted gradually by means of a low flame. With the aid of a suitable light, and a magnifier if necessary, the appearance of the deposited material on the slide may easily be observed. When the sublimation appears to be completed the cup section is disconnected and the slide is removed and placed in the special glass holder for examination under suitable power without the use of a cover-glass. Further observations and tests on the sublimed deposit may be carried out following the procedure described by Chamot.

Observations have been conducted for the purpose of determining the relation of the observed temperature in the air-bath to the actual temperature in the sublimator. At a bath temperature approaching 100°C., after approximately one-half hour heating, there is substantially no difference between the observed and the actual temperature inside the sublimator cup. A number of tests have shown that the temperature inside the cup is only a trifle lower than the observed temperature of the heating bath.

DOMESTIC SOURCES OF CANTHARIDIN.

I. *Macrobasis albida* Say.

By Arno Viehoever and Ruth G. Capen (Bureau of Chemistry, Washington, D. C.).

Cantharidin is the blistering principle occurring in certain beetles. The official source is limited to *Cantharis vesicatoria* (Linné) De Geer, Spanish or Russian flies. Another recognized source for cantharidin is *Mylabris cichorii* Fab., so-called Chinese flies. None of these forms occur in this country; consequently, material containing cantharidin, or cantharidin itself, is imported. In spite of the fact that blister beetles are known to occur in the United States, no domestic sources have, to the knowledge of the writers, been examined, either qualitatively or quantitatively, for the presence of cantharidin. The price of the material yielding cantharidin is comparatively high, Russian cantharides being quoted at $3.25 per pound, while Chinese flies are $1.10 per pound[1]. Cantharidin, which the United States Pharmacopœia Revision Committee contemplates making official, is not quoted in the open American market.

For these various reasons it seemed justifiable to make a survey of the domestic sources. This paper describes work done with one of the species of beetles, *Macrobasis albida* Say. (see Fig. 1), found to contain cantharidin.

[1] Drug and Chemical Markets, October 25, 1922.

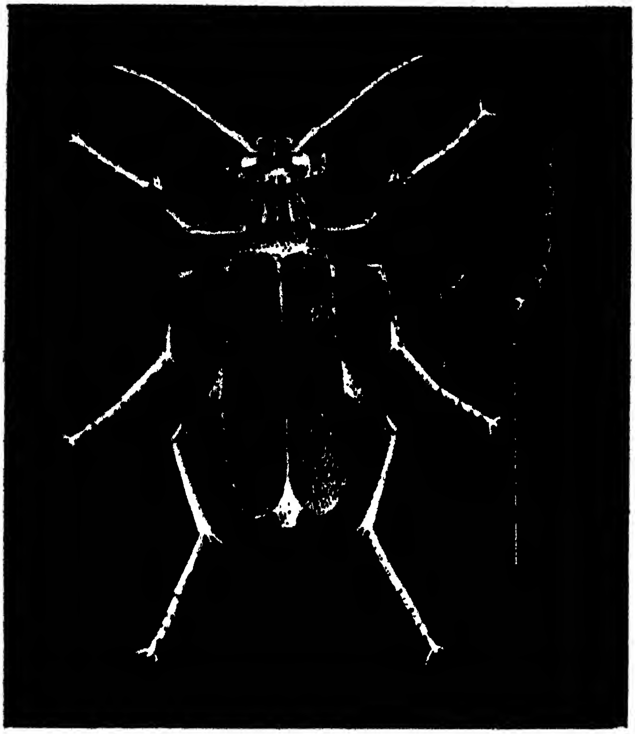


FIG. 1.—*Macrobasis Albida* Say. After Chittenden

ORIGIN AND NATURE OF THE MATERIAL.

Material for the work was obtained through the kindness of F. H. Chittenden, Truck Crop Insect Investigations, Bureau of Entomology.

The species *Macrobasis albida* Say., the "two-spotted blister beetle", belongs to the family *Meloidae.* It compares very well in size with the European *Cantharis vesicatoria.* It is gray, yellowish or brownish, unicolorous, or with markings. The prothorax usually has two longitudinal black stripes; the elytra are usually concolorous, sometimes with sub-marginal black stripes. The basal points of the antennae are brown.

This variety of beetle occurs abundantly in Texas, Kansas and adjoining states. *Macrobasis albida* and closely related species feed on legumes and other plants that root deeply, devouring the petals and pollen of the flowers. Irish potatoes and sugar beet plants are completely defoliated by the beetles[1].

ISOLATION OF CANTHARIDIN.

The beetles were carefully dried at a temperature not exceeding 70°C. Cantharidin was readily sublimed from very small amounts of the powdered material. Even larger amounts were obtained when the

[1] Milliken, F. B., U. S. Dept. Agr., Bull. 967, 1922, 2, 3, 5.

powder, before sublimation, was moistened with chloroform containing sufficient hydrochloric acid (10 per cent) to render it distinctly acid. The material was sublimed in a small apparatus[1] which was heated in an oil bath at temperatures from 110° to 120°C. A partial vacuum and a cooling device was used. Cantharidin was deposited on the cover slip in pure white plates, sometimes with a small amount of fat, which was readily removed with petroleum ether.

CHARACTERISTICS OF CANTHARIDIN.

Cantharidin has a melting point of 210°C., but sublimes as low as 100°. It forms a white substance which crystallizes in large plates.

OPTICAL PROPERTIES[2].

Angle of extinction = parallel.
Indexes—1.505 1.54.

SOLUBILITIES.

Soluble in	30,000	parts cold water [3], [5].
Soluble in	15,000	parts hot water [3], [5].
Soluble in	8,000	parts 1 per cent sulfuric acid[3].
Soluble in	2,500	parts carbon tetrachloride[4].
Soluble in	900	parts ether[3].
Soluble in	833	parts 45 per cent formic acid[4].
Soluble in	800	parts absolute alcohol[3].
Soluble in	715	parts 10 per cent acetic acid[4].
Soluble in	500	parts benzol[3].
Soluble in	65	parts chloroform[3], [5].
Soluble in	38	parts acetone[5].
Soluble in	245	parts 75 per cent acetone[4].
Soluble in	625	parts 50 per cent acetone[4].
Soluble in	5,000	parts 25 per cent acetone[4].

Selinite Test.

This test was carried out according to the method of Klein[6]. Concentrated sulfuric acid and a trace of sodium selinite added to the alcoholic cantharidine solution gave a slight purple color. Upon heating, the coloration gradually increased and changed to blackish, which, upon addition of alcohol, turned to a dark purple color.

Quantitative Experiments.

Dubois'[7] method was used, extracting both the free, and free and combined cantharidin. The method is as follows:

---

[1] Viehoever, Arno., *J. Assoc. Official Agr. Chemists*, 1922, 5: 557.
[2] Determined by J. F. Clevenger, Pharmacognosy Laboratory, Bureau of Chemistry, Washington, D. C.
[3] Rosenthaler, L., Der Nachweis organischer Verbindungen, 1914, 834.
[4] Seidell, A., Solubilities of Inorganic and Organic Compounds, 1919, 226.
[5] Schmidt, Ernst., Lehrbuch der Pharmaceutischen Chemie (Organische Chemie), II, Part II, 1911, 1926.
[6] *J. Ind. Eng. Chem.*, 1910, 2: 389.
[7] *Am. J. Pharm.*, 1920, 92: 157.

To 10 grams of dried powder passing through a 40-mesh sieve add 30 cc. of chloroform and allow to stand overnight. Then shake at short intervals during 2 or 3 hours. Filter and wash with 70 cc. of chloroform and evaporate the filtrate on water bath. Treat the residue with 5 cc. of carbon bisulfide and transfer to tared filter paper. Wash with 10 cc. of carbon bisulfide and dry at 60°C. Weigh material. Add 0.010 gram for solvent action. This should give free cantharidin. To obtain combined as well as free cantharidin follow the same procedure, except add 2 cc. of concentrated hydrochloric acid to the original chloroform.

The results obtained by this method are as follows:

	per cent	*per cent*
Free cantharidin	1.04	0.85
	0.80	0.67
Free cantharidin and cantharidin salts	3.92	3.83
	4.21	....

DISTRIBUTION OF CANTHARIDIN.

Female beetles are considered to be more valuable as a source of cantharidin than the male[1]. Various experiments have been made by subliming material consisting of different parts of the beetles. The eggs were found to be very rich in the active principle. The heads contained a smaller amount and the wings none. *Macrobasis albida*, yielding over 1 per cent free cantharidin and from 4 to 5 per cent free and combined cantharidin[2], contains as large, if not larger amounts of cantharidin than do the other varieties. *Cantharis vesicatoria* yields less than 1 per cent[3], and *Mylabris chicorii* from 0.426 to 1.362 per cent, or on an average 1.2 per cent[4].

SIGNIFICANCE OF FINDINGS.

The fact that the beetles occur abundantly in various middle western states and that they contain cantharidin far in excess of the minimum requirements of the U. S. Pharmacopœia, namely, 0.6 per cent, very strongly suggests their commercial value.

SUMMARY.

The beetle, *Macrobasis albida* Say, abundant in Texas and Kansas, was found to contain cantharidin.

The amounts of free cantharidin varied from 0.6 to 1 per cent; of cantharidin and cantharidine salts from 4 to 5 per cent.

The eggs were found to contain large amounts; the heads, very small amounts; and the wings, no cantharidin.

Macrobasis albida, American blister beetles or American blister flies, represent a possible domestic commercial source of cantharidin.

[1] Sanders, Wm. *Proc. Amer. Pharm. Assoc.*, 1876, 24: 509.
[2] Determined by Ruth G. Capen.
[3] Juritz, C. F. *S. African J. Industries*, 1919, 2: 470.
[4] Ewe, Geo. E. *J. Am. Pharm. Assoc.*, 1920, 9: 260.

QUANTITATIVE DETERMINATION OF ACETIC ANHYDRIDE[1].

By G. C. Spencer (Analytical Reagent Investigations Laboratory, Bureau of Chemistry, Washington, D. C.).

Previous methods are briefly reviewed. The proposed method is based upon the reaction of acetic anhydride and aniline dissolved in cold chloroform. An equivalent amount of acetanilide forms. Attempts made to separate and weigh acetanilide proved unsatisfactory. The acetanilide is hydrolyzed by sulfuric acid and the resulting aniline sulfate is titrated with bromate-bromide solution.

The methods that have been proposed for the quantitative estimation of acetic anhydride may be grouped under three heads: (1) Direct titration; (2) extraction with a solvent; (3) separation of a derivative which may be weighed or titrated.

(1) The United States Pharmacopœia (9th edition, page 522) directs that 10 cc. ("mils") of acetic anhydride be accurately weighed and made up to 100 cc. with water. Ten cc. of this solution are titrated with normal alkali. Not less than 19.3 cc. are required to neutralize 1 gram of acetic anhydride. The U. S. P. requirement therefore indicates 90 per cent or more of the anhydride.

A method given in Beilstein's[2] recommends boiling a weighed quantity of acetic anhydride with an excess of normal sodium hydroxide and titrating back with 0.1N acetic acid. Expressed as acetic acid, each per cent of acidity in excess of 100 corresponds to 5.67 per cent of acetic anhydride.

(2) The one method found in the literature that depends upon extraction with a solvent is that proposed by Wolgast[3]. Exactly 25 cc. of water are shaken with a solution of 25 cc. acetic anhydride in 30 cc. of benzene for 15 seconds and allowed to separate. The acetic anhydride remains dissolved in the benzene while the acetic acid is dissolved by the water. The increase in the volume of the water layer in cubic centimeters multiplied by 4 gives the percentage of acetic acid in the sample.

It may be explained here that acetic anhydride does not react as readily with water as do the anhydrides of many inorganic acids.

(3) The literature describes two procedures based upon the formation of a derivative such as acetanilide. One of these is stated by its origi-

[1] Presented at the 64th meeting of the American Chemical Society, Pittsburgh, Pa., Sept. 4–8, 1923.
[2] Handbuch der organischen Chemie, 1920, vol. II, 169.
[3] *Svensk Kem. Tid.*, 1920, 32: 10.

nators to be applicable only to high concentrations of anhydride in acetic acid, and the other is recommended only for low concentrations in the same acid.

The first is the method of Menschutkin and Wasilieff[1]. It is recommended by them for solutions containing over 60 per cent of anhydride in acetic acid. The sample is treated with aniline, which reacts with the anhydride to form aniline acetate and acetanilide in molecular proportions, and with the free acetic acid to form aniline acetate. The total aniline acetate is titrated directly with standard barium hydroxide solution, using phenolphthalein as an indicator. The results have been found by the writer to be satisfactory.

The second of these methods has been published by Edwards and Orton[2], who state that it is applicable only to low percentages of anhydride in acetic acid. The anhydride is caused to react with 2, 4-dichloroaniline at 16°C. This reaction forms equivalent quantities of dichloroacetanilide and dichloroaniline acetate. An unstable chlorine derivative is made by treating the dichloroacetanilide with bleaching powder solution. This compound reacts with potassium iodide to liberate an equivalent amount of iodine which is titrated with sodium thiosulfate solution. The writer's experience with this method leads to the belief that while it may be accurate in the hands of experienced workers, it nevertheless involves a number of reactions and requires the use of large volumes of solution.

The writer's experience with the preceding methods has been unsatisfactory, except as noted.

H. E. Buc, formerly of the Bureau of Chemistry, suggested tentatively that acetic anhydride be assayed by dissolving in ether a weighed quantity of the sample, adding an excess of aniline to form acetanilide and aniline acetate, extracting the acetanilide with chloroform, evaporating the solvent, drying, and weighing. From this weight the amount of acetic anhydride is calculated. This procedure served as a basis of the method about to be proposed.

EXPERIMENTAL WORK.

Blanks on chloroform and aniline alone.—1.5 cc. of aniline was dissolved in 15 cc. of chloroform, and the solution was transferred to a Squibb separatory funnel with 10 cc. more of chloroform. Ten cc. of 10 per cent sulfuric acid and 15 cc. of water were added, the mixture was shaken well, and the liquids were allowed to separate. The chloroform layer was drawn into a second separatory funnel containing 15 cc. of water. After shaking, the chloroform layer was allowed to separate

[1] *J. Russ. Phys. Chem. Soc.*, 1896, **21**: 190.
[2] *J. Chem. Soc.*, 1911, **99**: 1181.

and was then drawn into a 200 cc. Erlenmeyer flask through a small dry filter. The aqueous residues in the two funnels were further extracted in succession, first with 10 cc. and then with 7 cc. of chloroform. These extracts were drawn into the Erlenmeyer flask. Ten cc. of 10 per cent sulfuric acid were added, and the flask was placed on a steam bath at moderate temperature until the chloroform had been expelled and the acid solution reduced to 4 or 5 cc. Ten cc. of water were added, and the evaporation was repeated. The practice here described may reasonably be questioned. In fact, it has since been abandoned, but, so far as the writer observed, no frothing or spurting occurred in this case. To the residue in the flask were added 60 cc. of water and 5 cc. of concentrated hydrochloric acid. This solution was titrated with half-normal potassium bromate-bromide solution. The results shown in the table indicate that some of the aniline in the form of sulfate was taken up by the chloroform, since no acetic anhydride or even acetic acid was present to form any acetanilide. Small amounts of tribromoaniline were observed as a flocculent precipitate after the titration.

Blanks on glacial acetic acid.—To 1.5 cc. of aniline, dissolved in 15 cc. of chloroform was added 0.3–0.8 gram of glacial acetic acid, and the solution was allowed to stand for 1 hour. The determination was carried out as already described. The results are given in the table as the apparent equivalent content of acetic anhydride in the acetic acid. It is uncertain whether a small amount of acetic anhydride is actually present in glacial acetic acid, or whether the action of the acetic acid on aniline is sufficient to form a small amount of acetanilide at low temperatures in dilute solutions.

As shown in the table, "edible" acetic acid (that made from calcium carbide) shows an apparent anhydride content lower than in commercial c. p. acetic acid. The effects of small amounts of water and of alcohol on the reaction showed that these did not appreciably affect the results. The blank on 90 per cent acetic acid was fairly comparable with that obtained on glacial acetic acid. The results have been corrected by subtracting the values for the chloroform and aniline blank in each case.

REAGENTS.

(a) *Sulfuric acid, 10 per cent.*

(b) *Aniline, freshly redistilled.*

(c) *Chloroform, U. S. P.*

(d) *Potassium bromate-bromide solution.*—Either dissolve appropriate quantities of the two salts in water or make up as follows: Dissolve 28 grams of potassium hydroxide in 300-400 cc. of water and from a buret in a hood add slowly and with stirring 13.3 cc. (40 grams) of bromine. Warm the mixture gently until the bromine has completely dissolved, then raise the temperature to the boiling point. Continue to boil for 5–10 minutes and if necessary add a little more potassium hydroxide to take up the last of the bromine. After cooling, make up to 1 liter. Standardize this solution as follows:

Weigh 0.3 gram of recrystallized acetanilide into a 200 cc. Erlenmeyer flask and add 10 cc. of 10 per cent sulfuric acid. In the same manner as directed in the next paragraph, proceed with the hydrolysis and titration. Ascertain the acetic anhydride factor by dividing the acetanilide weight (in grams) by the volume of bromate-bromide (in cubic centimeters) and multiplying this quotient by 0.7555. A solution thus prepared is approximately half-normal.

DETERMINATION.

Weigh 0.3–0.4 gram of the acetic anhydride sample in a small glass capsule, fitted with a well-ground glass stopper. Add the capsule containing the charge to a cooled mixture of 15 cc. chloroform and 1 cc. of aniline contained in a 100 cc. glass-stoppered Erlenmeyer flask. The capsule is most conveniently opened by holding it in the neck of the inclined flask, removing the stopper, and allowing both parts to slide into the chloroform. Stopper the flask immediately, mix thoroughly, and leave the flask in the refrigerator for not less than 1 hour.

Rinse the chloroform solution of the charge into a 125 cc. Squibb separatory funnel containing 15 cc. of 10 per cent sulfuric acid and 15 cc. of water, using 10 cc. more of chloroform. Shake well and allow to separate. Draw the chloroform layer into a second separatory funnel containing 15 cc. of water. Shake this mixture, and after the layers have separated draw the chloroform into a 200 cc. Erlenmeyer flask through a small dry filter. To the first separatory funnel add 10 cc. of chloroform. Shake well and draw the lower layer into the second separatory funnel, shake, and pass the chloroform into the Erlenmeyer flask through the same filter. Repeat the extractions with 7 cc. of chloroform. Evaporate or distil cautiously the greater part of the chloroform from the combined extracts and drive off the remainder of the solvent by a gentle air blast.

Add 10 cc. of 10 per cent sulfuric acid to the crystals in the Erlenmeyer flask. Allow it to evaporate slowly on the steam bath until the volume is reduced about one-half. Add 10 cc. of water and repeat the evaporation. Care must be used to insure complete hydrolysis of the acetanilide, but the acid must not become so concentrated that it will decompose the aniline sulfate. Take up with 60 cc. of water, add 5 cc. of concentrated hydrochloric acid, and titrate the solution with the potassium bromate-bromide solution. The liberated bromine reacts with the aniline sulfate to form s-tribromo-aniline which separates as a white flocculent solid. The end-point is the yellow tinge that appears in the solution as soon as the bromine is in excess and must be approached very carefully.

1 cc. 0.5N $KBrO_3-KBr$ = 0.008505 gram acetic anhydride.

Greater accuracy is attained by using fifth-normal potassium bromate-bromide solution when only small amounts of acetic anhydride are present.

The reactions are expressed as follows:

$2\ C_6H_5NH_2+(CH_3CO)_2O=C_6H_5NHCOCH_3+C_6H_5\ NH_3\ O_2\ C_2\ H_3.$

$C_6H_5NHCOCH_3+H_2O+\frac{1}{2}\ H_2SO_4=C_6H_5NH_2\ \frac{1}{2}\ H_2SO_4+CH_3CO_2H.$

$C_6H_5NH_2\ \frac{1}{2}\ H_2SO_4+6\ Br=C_6H_2Br_3\ NH_2\ \frac{1}{2}\ H_2SO_4+3\ H\ Br.$

The table summarizes the collaborative work of five chemists. Samples 11 to 29 are the same commercial acetic anhydride. The mean of all these results is 90.78 per cent.

Two of the collaborators were inexperienced in the method, and two others only slightly experienced.

The nature of acetic anhydride and the difficulties attending its preparation in a state of absolute purity render the confirmation of any analytical method more or less uncertain.

Analytical Results.

(1 cc. 0.5N. $KBrO_3-KBr$ solution = 0.008505 gram acetic anhydride.)

Sample No.	Material Examined	Weight Taken	0.5N Standard Solution	Acetic Anhydride	
		gram	*cc.*	*gram*	*per cent*
1	Blank on aniline	.....	0.26	0.00221	.....
2	Blank on aniline	.....	0.25	0.00212	.....
3	Glacial acetic acid	0.4045	0.30	0.00255	0.63
4	Glacial acetic acid	0.3598	0.34	0.00289	0.80
5	3 and 4 reduced to	0.2646	0.13	0.00110	0.41
6	90 per cent acid strength	0.2742	0.11	0.00093	0.33
7	"Edible" acetic acid	0.3103	0.07	0.00059	0.13
8	"Edible" acetic acid	0.3366	0.04	0.00034	0.10
9	4 per cent solution in	0.5262	2.36	0.02007	3.81
10	glacial acetic acid	0.5742	2.46	0.02092	3.64
11	Commercial acetic anhydride	0.4772	50.48	0.4293	89.97
12	Commercial acetic anhydride	0.4145	44.27	0.3765	90.84
13	Commercial acetic anhydride	0.4021	42.05	0.3576	88.94
14	Commercial acetic anhydride	0.2976	31.67	0.2693	90.51
15	Commercial acetic anhydride	0.3644	39.03	0.3319	91.08*
16	Commercial acetic anhydride	0.3494	37.29	0.3171	90.75*
17	Commercial acetic anhydride	0.5105	55.08	0.4684	91.75†
18	Commercial acetic anhydride	0.5620	61.09	0.5196	92.45†
19	Commercial acetic anhydride	0.4480	47.64	0.4052	90.44†
20	Commercial acetic anhydride	0.5417	58.51	0.4976	91.86†
21	Commercial acetic anhydride	0.3705	39.53	0.3362	90.74‡
22	Commercial acetic anhydride	0.3136	33.52	0.2851	90.91‡
23	Commercial acetic anhydride	0.3610	38.58	0.3281	90.89‡
24	Commercial acetic anhydride	0.3579	38.58	0.3281	91.78‡
25	Commercial acetic anhydride	0.3626	38.86	0.3305	91.15§
26	Commercial acetic anhydride	0.4268	44.99	0.3826	89.64§
27	Commercial acetic anhydride	0.3496	37.20	0.3164	90.50§
28	Commercial acetic anhydride	0.3650	38.75	0.3295	90.29§
29	Commercial acetic anhydride	0.3118	33.13	0.2817	90.37§

*Results by W. F. Baughman.
†Results by J. K. Morton.
‡Results by R. M. Hann.
§Results by J. I. Palmore.

SUMMARY.

A volumetric method for determining acetic anhydride which applies equally well so far as experience shows to high and low concentrations in acetic acid is described.

The estimation is readily effected without using unusual or expensive chemicals or apparatus.

The results obtained indicate for the method an accuracy within one per cent.

CONTRIBUTED PAPERS.

THE EFFECT PRODUCED UPON THE FAT OF HOGS BY FEEDING FISH MEAL.

By JAMES B. MARTIN (Bureau of Animal Industry, Washington, D. C.).

Fish meal[1] is a commercial product obtained by cooking, pressing and drying wholesome, undecomposed, raw fish material, under sanitary conditions. Its principal constituents are protein and fat. Feeding experiments have shown it to be a valuable supplementary feeding stuff and have failed to confirm the assumption that the feeding of fish meal of good quality as a supplementary feed in connection with other feeds imparts a fishy taint to the meat of the hogs or to the lard rendered from their fat.

Frank G. Ashbrook[2], of the Bureau of Animal Industry, conducted experiments at the Experimental Farm of the Bureau at Beltsville, Maryland, to determine, first, the comparative values of fish meal and tankage as supplements in a ration for growing and fattening pigs; and second, the value of dried pressed potato in a ration for fattening hogs when supplemented by feeds rich in protein.

Under the first experiment, the feeding period was divided into two parts: (1) a growing period; and (2) a finishing period. During the first period the pigs were divided into two lots of eight and four and fed on the following rations:

Lot 1 ration: 4 parts corn meal, 4 parts middlings, 1 part tankage.
Lot 2 ration: 4 parts corn meal, 4 parts middlings, 1 part fish meal.

During the second period the pigs were divided into 3 lots of four and fed on the following rations:

Lot 3 ration: 4 parts corn meal, 4 parts middlings, 1 part fish meal.
Lot 4 ration: 9 parts corn meal, 1 part fish meal.
Lot 5 ration: 9 parts corn meal, 1 part tankage.

Under the second experiment, the pigs were divided into four lots of three pigs each and fed on the following rations:

Lot 1 ration: 6 parts corn meal, 1 part tankage.
Lot 2 ration: 6 parts dried pressed potato, 1 part tankage.
Lot 3 ration: 6 parts dried pressed potato, 1 part linseed oil meal (old process).
Lot 4 ration: 6 parts dried pressed potato, 1 part fish meal.

[1] U. S. Dept. Agr. Bull. 378.
[2] *Ibid.*, 610.

The analysis of the fish meal was as follows:

	per cent
Water	6.36
Fat	15.34
Protein (N×6.25)	57.31
Ash	16.52
Undetermined	4.47

The results of these experiments showed conclusively that fish meal is a very effective supplement to a grain ration for pigs, that it is superior to tankage in all comparisons, that it is an outstanding protein supplement to feed along with potatoes, and that where it can be obtained conveniently at a reasonable price it is of considerable value in hog feeding. In addition, pigs relish it and maintain a thrifty growth. These experiments also showed that fish meal does not impart a fishy flavor to the meat or lard if it is fed in proper proportions with other feeds. At the conclusion of both these experiments the fresh pork from one of the hogs was eaten by individuals who were ignorant of the feed that the hogs had been given. Lard was also rendered from both the trimmings and the carcass, and observations were made. In no case was the meat reported as having a fishy odor or taste, neither was it evident in the rendering of the lard.

Four samples of the lard rendered from hogs fed on fish meal were sent to the Meat Inspection Laboratory for chemical examination and came under the observation of the writer. The lard was very white in color and had an agreeable taste and normal odor; no fishy odor or flavor could be distinguished. Approximately 50 grams of this lard and 50 grams of a normal prime steam lard were heated simultaneously over a Bunsen burner to a temperature of 176°C., and up to this temperature neither sample gave any evidence of a foreign or an offensive odor. Heating was discontinued at this point as both samples began to smoke and give off the characteristic acrid fumes of overheated fat. The regular laboratory methods for testing a lard chemically for its identification were next applied to both lards, and the following results, which are practically identical, were obtained:

	LARD FROM HOGS FED ON FISH MEAL	PRIME STEAM LARD
Color	White	White
Halphen test	Negative	Negative
Per cent of free acid	0.11	0.17
Iodine No.	62.86	63.15
Melting point of stearine crystals	64°C.	64.2° C.

The samples were then tested for the presence of glycerides of the characteristic fatty acids of fish oils. Fish and marine animal oils differ from other fats in that they contain glycerides of certain highly unsaturated acids which have the property of forming insoluble brom-

addition compounds. This property is the basis of a sensitive method for the detection of fish oils in animal and vegetable oils. The lard was first tested by the official method[1] for the detection of fish and marine animal oils in animal and vegetable fats. This test consists in dissolving a portion of the suspected fat in a mixture of chloroform and glacial acetic acid, adding an excess of bromine and allowing to stand for a brief period of time in boiling water. Vegetable and animal fats remain clear, but if fish fat is present there is a precipitate due to the formation of the insoluble brom-addition compounds. When tested by this method a small but distinct and unmistakable precipitate was observed in each sample.

The samples were further examined for the presence of clupanodonic acid. This acid, $C_{17}H_{27}COOH$, has been isolated from fish and marine animal fats by several observers and is the characteristic acid of those fats. It is capable of taking up eight atoms of bromine, thereby forming octo-brom stearic acid. The latter compound is insoluble in ether and other organic solvents. It may be readily separated from the brom-addition products of the other unsaturated acids, all of which are soluble in warm ether. When separated, it may be distinguished by the fact that it does not have a definite melting point but decomposes at temperatures of 200°C., or thereabout, without melting.

The fatty acids were prepared by the following method:

Approximately 100 grams of the lard were mixed with 200 cc. of alcohol distilled over sodium hydroxide in a large Erlenmeyer flask and let stand on the steam bath until the boiling point was nearly reached. At the same time 30 grams of potassium hydroxide were dissolved in water, mixed with 150 cc. of alcohol, placed on the steam bath and heated nearly to the boiling point. When the contents of each flask were nearly at the boiling point the alcoholic potash was added to the flask containing the fat. Saponification was immediate and complete. The soap solution was evaporated to dryness and dissolved in 400 cc. of water. The fatty acids were then set free by adding an excess of sulfuric acid in 5% solution and washed four times with distilled water, 300 cc. being used for each washing. They were next dissolved in 500 cc. of a mixture of glacial acetic acid and ether in equal parts, and a solution of bromine in glacial acetic acid was added until the color of the bromine persisted. This action was carried out at a temperature ranging from 5 to 8°C. The solution was held in a refrigerator at a temperature of not over 12°C. for 18 hours. A white precipitate of powdery or sandy character was formed. The clear supernatant liquid was then decanted off and the precipitate washed with ether and dried.

The precipitate was hard, brittle and rather easily broken up to a fine white or gray powder, having the appearance of fine white sand. It was insoluble in all organic solvents tried. When determination of its melting point was attempted it decomposed at 186°C. As a check, a portion of the prime steam lard used for comparison, as well as several other samples of lard, was saponified, and the fatty acids were bromi-

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 256

nated in the same way. No precipitate of brominated acids insoluble in cold ether was obtained.

The percentage of bromine in the precipitate was next determined. A weighed portion was placed in an ignition tube with approximately four times its weight of a mixture consisting of equal parts of calcium oxide, sodium carbonate and potassium nitrate and cautiously ignited until the substance decomposed. The temperature was then raised until the carbon was all burned off, leaving a white mass in the tube. The tube was shattered by dropping it while still hot into a beaker containing water, and the mass was dissolved in dilute nitric acid and filtered. Bromine was determined in the filtrate in the usual way. The results of the first test showed 62.94 and 62.59 per cent bromine in duplicate samples. This percentage is considerably below the theoretical percentage of bromine in octo-brom stearic acid, which is 69.84 per cent. As the fatty acid had been allowed to stand overnight on the steam bath, it appeared probable that there had been oxidation of a portion of the clupanodonic acid. The experiment was, therefore, repeated, the fatty acids being brominated as soon as prepared. Duplicate determinations of bromine in the precipitate yielded 68.8 and 67.9 per cent of bromine. While the percentage of bromine found does not agree exactly with the theoretical, it is believed that the discrepancy is due to the possible presence of small amounts of impurities in the precipitate, and that the bulk of the precipitate consisted of octo-brom stearic acid derived from the clupanodonic acid present in the fat. Quantitative determination of brominated acids in one experiment gave a yield of 0.15 per cent, corresponding to 0.045 per cent of clupanodonic acid in the lard.

SUMMARY AND CONCLUSIONS.

The fat of hogs fed on fish meal has been found identical with normal fat in its physical aspects and ordinary chemical characteristics.

The fat of hogs fed on fish meal has been found to contain a small proportion of the glyceride of clupanodonic acid.

Clupanodonic acid has been identified by the preparation of insoluble octo-brom stearic acid having the known properties of that substance and containing nearly the theoretical percentage of bromine.

NUT MARGARINES.

By J. T. KEISTER (Food Control Laboratory, Bureau of Chemistry Washington, D. C.).

INTRODUCTION.

According to Clayton[1], Hoffman[2] first suggested the use of nut oils in the manufacture of margarine. A patent was issued to Meinert and Jeserich[3] for the manufacture of this product exclusively from vegetable oils, and in 1896 the use of coconut oil, which has become the chief constituent of this product, was patented by Ruffin[4].

From a purely scientific standpoint, several important advances have been made in margarine manufacture since the invention of the French chemist, Mège-Mourie, in 1869. First may be mentioned the use of cultures of lactic acid organisms for souring the milk used in churning the fats to impart a butter flavor to the product; second, the introduction of vegetable oils and fats, leading to the class of products known as nut margarines, which class is the subject of this paper. A third improvement was the introduction of the hardened (hydrogenated) oils, the use of which assists in regulating the melting point of the margarine fat, thereby producing a product more resistant to temperature conditions than would be the case without such hydrogenation. It may be stated, therefore, that the entire process of the manufacture of nut margarine is based upon scientific principles.

RAPID GROWTH OF THE NUT MARGARINE INDUSTRY.

The manufacture of nut margarine appears to have begun in this country early in the year 1917. The first figures available[5], for the month of February, show a total production of 608,330 pounds, and for the entire year, a total production of approximately 22,000,000 pounds, which represented about 2½ per cent of the total margarine produced. The production for the month of February alone, in 1918, was over 9,500,000 pounds, about 25 per cent of the total production, and nearly 16 times greater than the production in the same month in 1917.

In September, 1919, the production of nut margarine is shown to have been about 28 per cent of the animal variety (oleomargarine); for the month of October it had increased to about 73 per cent; for the month of December the production of the two products was almost equal in amount; and in May, 1920, statistics show that the production of vegetable or nut variety exceeded that of the animal variety, being 20,972,644 and 19,962,711 pounds, respectively.

[1]Margarine, 1920, 4.
[2] Eng. Pat. 3867, 1880.
[3] *Ibid.*, 915, 1880.
[4] *Ibid.*, 1827, 1896.
[5] *Amer. Food. J.*, 1918, 13: 207.

The number of factories producing nut margarine in the United States increased from three in April, 1917[1], to over 60 in December, 1920[2].

REASONS FOR THIS INVESTIGATION.

Nut margarine being a comparatively new food product, it was necessary to secure information as to its manufacture and composition, also to determine whether the present analytical methods used for butter were adequate and applicable to this product, and to develop and apply new methods where necessary.

A sufficient number of factory inspections were made to get a general knowledge of the materials used, the methods of treatment and the processes followed in the manufacture of the margarine. All samples were collected by the writer in Washington, where many different brands of the product are on sale.

MATERIALS USED AND PROCESS OF MANUFACTURE.

Different kinds of oil and either skimmed or whole milk form the basis for the manufacture of this product in the United States. The principal oils used are coconut and peanut oils which have been properly refined and deodorized. Other vegetable oils, such as cottonseed and sesame, have been found present in small quantities.

In order to obtain a margarine which has the desired consistency (softening and melting points), various proportions of hydrogenated and untreated oils are employed. The proportions used depend not only on the degree of hydrogenation of the hardened fat, but also upon the season of the year. It is customary during the warm weather to prepare margarine which contains a somewhat larger quantity of hardened fat. Pickard[3] estimates that the amount of untreated oil used varies from 5 to 25 per cent.

Whole or skimmed milk, ripened to 0.6 to 0.7 per cent lactic acid, is added, and the mixture, at a temperature of about 68°F., is put into large barrel-shaped revolving churns or mixers. The essential element in preparing the cultured milk is temperature control; the heat should not be raised so high as to change the physical properties and flavor of the milk, nor should it be too low for proper bacterial growth. According to Pickard, "the fundamental principle of the churning operation is to form an emulsion of the milk with the oil in order that the utmost degree of contact of the two may be brought about * * * so that the effect of the one upon the other is at a maximum. The temperature of the liquid must be closely watched, and the operation stopped at the

[1] The Market Reporter, U. S. Bur. Markets, April 3, 1920.
[2] *Ibid.*, January 15, 1921.
[3] *Amer. Food J.*, 1918, 13: 16.

time when the emulsion is most perfect". From the mixers the emulsion flows through a pipe to the floor below and is deposited in a thin film upon the surface of hollow revolving cylinders, which are chilled by the circulation of cold brine through them. By the proper application of scraping knives to the surface of the cylinders, the solidified emulsion is scraped off directly into tempering trucks. These trucks, containing the fat, are stored in a cool room for 24 hours while the product "ripens"; this process is claimed to give the finished article the proper flavor. The product then goes to a machine where water is worked out and the salt added and worked in, as in the case of butter. From the worker the product is placed in trucks, and from these it is transferred by means of wooden scoops to a hopper which leads to the moulding or printing machines. The margarine comes from the moulds in a continuous flat block from which one-pound—or larger—prints are cut by wires; it is then packed in cartons either by hand or by machinery. Weights are occasionally checked up to insure full weight.

METHOD OF ANALYSIS.

As seen from the attached table, water was determined both by the official method[1], and by Patrick's "rapid beaker" method[2], with slight modifications. The latter method consists in weighing out accurately about 5 grams of the prepared sample into a dry aluminum or silica beaker, driving off the moisture by heating over a burner (low flame), using a wire beaker holder, revolving gently and removing from flame, if necessary, to avoid loss by sputtering. When the sample ceases to foam and the curd assumes a light-brown color, it is removed from the source of heat; the beaker is cooled in cold water, and all moisture adhering is carefully wiped off; the sample is weighed, and from the loss in weight the percentage of moisture in the sample is calculated. It will be noted from the results recorded in the table that checks in fairly good agreement with the official method were obtained in most cases by this method. It should be stated that the principal difficulty in determining moisture in nut margarine is in obtaining a uniform sample; this appears to be more difficult than in the case of butter.

Fat was determined by the official (indirect) method[3]. Casein and salt were also determined by the A. O. A. C. methods[4], the volumetric silver nitrate method being used, with potassium chromate as indicator.

EXAMINATION OF THE FAT.

The following methods were used: for refractive index, free fatty acids, Reichert-Meissl number, Polenske number and saponification

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 232.
[2] *J. Am. Chem. Soc.*, 1907, **29**: 1126.
[3] *Assoc. Official Agr. Chemists, Methods*, 1920, 232.
[4] *Ibid.*, 233.

number, the regular official methods[1], the Leffman and Beam method being applied for the Reichert-Meissl number; for the iodine number, the Wijs procedure[2], with approximately one gram of the sample; for the melting point of the fats, the capillary tube method[3], as recommended by the Committee on Analysis of Commercial Fats and Oils of the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society; for cottonseed oil the official Halphen test[4]; for sesame oil, the Baudouin and Villavecchia tests[4]; and for peanut oil, Bellier's qualitative test[5].

Bellier's method is essentially as follows:

Saponify 1 gram of the oil with 5 cc. of alcoholic potash solution (4.25 grams of potassium hydroxide, purified by alcohol and containing about 87% of potassium hydroxide, dissolved in 70% alcohol and made up to 50 cc.) by gentle heat until clear. Add 1.5 cc. of an acetic acid solution of such strength that the 1.5 cc. will exactly neutralize the 5 cc. of alcoholic potash solution. Cool in water at 18°C. for at least 30 minutes, with occasional shaking. To the solution in the tube, add 50 cc. of 70% alcohol containing 1 cc. of concentrated hydrochloric acid per 100 cc., mix the whole and place in water at 18°C. If peanut oil is present in amounts of 5%, or more, a distinct precipitate is formed, the volume of precipitate increasing with the percentage of oil present.

The question of determining peanut oil quantitatively was given considerable attention, and some results were obtained and reported on the last eight samples as shown in the tabulation. This work was based upon the work of Bellier[6], as modified by M. Mansfield[7], Adler[8] and Evers[9]. The method:

Weigh 5 grams of sample into a flask, saponify with 25 cc. of alcoholic potash (80 grams of potassium hydroxide dissolved in 80 cc. of water and diluted to 1000 cc. with 90% alcohol) by heating under a reflux condenser for 5 minutes. To the hot soap, add 7.5 cc. of acetic acid (1 volume of glacial acetic acid to 2 volumes of water) and 100 cc. of 70% alcohol containing 1 cc. of concentrated hydrochloric acid per 100 cc.; cool to 12°-14°C. for 1 hour. Filter and wash with 70% alcohol containing 1 cc. of concentrated hydrochloric acid at a temperature of 17°-19°C., breaking up the precipitate occasionally with a platinum rod; continue the washing until the filtrate gives no turbidity with water (the washings being measured). Dissolve the precipitate according to its bulk in 25-70 cc. of hot 90% alcohol and cool to a temperature of 15° to 20°C. If crystals appear in any quantity allow to stand at this temperature from 1 to 3 hours; filter and wash with a measured quantity of 90% alcohol (about one-half the volume used for crystallization) and finally with 50 cc. of 70% alcohol. Wash the crystals with warm ether into a weighed flask; evaporate off the ether, dry at 100°C., and weigh. In case no crystallization is effected with 90% alcohol reduce the strength to 70%. Correction is made for the solubility of the mixed fatty acids in 70% alcohol, depending upon the volume used for washing and also upon the weight of the fatty

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 241-250.
[2] *Ibid.*, 245.
[3] *J. Ind. Eng. Chem.*, 1919, 11: 1165.
[4] *Assoc. Official Agr. Chemists, Methods*, 1920, 253-254.
[5] Bolton and Revis. Fatty Foods, 81.
[6] *Ann. Chim. anal.*, 1899, 4: 4.
[7] Die Untersuchung der Nahrungs-Und Genussmittel., 2ud ed., 1905, 57.
[8] *Zeit.-Nahr. Genussm.*, 1912, 23: 676.
[9] *Analyst*, 1912, 37: 487.

acids obtained. Evers used the factor 20 for fatty acids having a melting point of 72°C. and 22 for a melting point of 73° to convert to percentage of peanut oil.

Bellier[1], in his work with pure peanut oil, found the factor 23.8 to give nearer a 100 per cent recovery. The experience of the writer would indicate that this factor of 23.8 is preferable, and it was used in calculating the results here reported. It is evident, however, that due to the impurity of the mixed fatty acids obtained, and also to natural variations in the content of arachidic and lignoceric acids present in oils from different sources and methods of treatment, no factor that may be selected would in every case give 100 per cent recovery.

Since the work on peanut oil reported in this paper was done, an improved method for the determination of peanut oil has been reported in a paper by Thomas and Chai-Lan Yu[2], entitled "The Determination of the Mixture of Arachidic and Lignoceric Acids in Peanut Oil by Means of Magnesium Soaps".

DISCUSSION OF RESULTS.

When this work was begun, judging from the experience of others, it was thought that difficulty would be met in determining accurately the percentage of water in nut margarine, owing principally to the presence of large quantities of coconut oil. The experience of the writer has shown this not to be the case, provided the sample is reasonably fresh.

Further work upon the method for the quantitative determination of peanut oil seems essential in case it is necessary to determine the proportion of the different oils present. By determining the percentage of peanut oil present by Evers' method the percentage of coconut oil could be obtained by difference, provided the oils used consisted only of coconut and peanut, which seems to be the usual practice at present.

From a review of the tabulated results, considerable variation in composition and proportion of the fats used is noted, as is indicated by a comparatively wide range in the refractive index and also in the melting point and iodine number of the fats, the two latter figures being an index of the degree of hydrogenation and proportion of hydrogenated oil used. Considerable variation in the Polenske number is also noted; this number is an index of the amount of coconut (or palm oil) present.

It is interesting to note that Sample No. 4311 gave a strong test for sesame oil, while another sample of this brand was examined for this oil with negative results.

It will be noted also that large quantities of cottonseed oil were found to be present in two samples and small amounts in four other samples. In several other cases a slight color was obtained which, no doubt, was due to cottonseed oil introduced by contamination from the machinery

[1] *Ann. Chim. anal.*, 1899, 4: 4.
[2] *J. Am. Chem. Soc.*, 1923, 45: 113.

Analyses of Nut Margarines.

SAMPLE NO.	WATER BY BEAKER METHOD	WATER BY OFFICIAL METHOD	FAT (indirect method).	CURD	ASH (including salt)	SODIUM CHLORIDE	FREE ACID AS OLEIC	CONSTANTS OF THE FAT: Refractive Index at 40°C.	Melting Point	Reichert-Meissl Number	Polenske Number	Saponification Number	Iodine Number (Wijs)	Calculated Peanut Oil (Evers-Modification of Bellier's Method (a))	(b) Melting Point of Fatty Acids Obtained in (a)	QUALITATIVE TESTS*: Bellier's test for Peanut Oil	Halphen test for Cottonseed Oil	ESTIMATED COTTON-SEED OIL
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	°C.	°C.					per cent	°C.			per cent
4311	12.48	12.41 12.62	84.55	0.61	2.09	2.03	0.34	38.1	31–32	5.73	9.16	237.4	13.54	. . .	. . . . . .	Positive	Negative	. . . .
4347	10.57 10.60 10.72	10.04 10.23	85.79	1.25	2.53	2.43	0.29	38.4	42–45	5.84	13.35	229.8	15.77	. . . . .	. . . .	Positive	Negative	. . . .
4372	11.67 11.71 11.84	11.68 11.71	83.14	1.60	3.58	3.59	0.177	39.7	35–36	5.11 5.16	11.82	232.1	15.92	. .	. . . . . .	Positive Weak	Positive	15
4381	11.40 11.47 11.51	11.60 11.79 11.78	84.87	0.995	2.68	. . . .	0.159	40.9	29–29.5	4.93	11.86	228.2	21.66 21.68	. . .	. . . .	Positive	Negative	. . . .
4404	13.07 13.13 13.47	13.50 13.55	83.49	1.42	1.56	. . . . .	0.142	38 5	24.6–24.8	5.22 5.44	13.12	252.1	12.50	. . . .	. . . . . .	Positive	Negative	. . . .
4419	10.93 10.97	10.98 10.97 10.86	82.62	1.52	4.96	. . .	0.087	40.7	25.2–25.7	4.94	13.11	232.4	20.57	. . . .	. . . .	Positive	Positive	5
4464	10.60 10.45	10.78 10.63 10.58	85.90	0.93	2.51	. . . . .	0.17	38.5	25.6–26	5.18	13.65	237.0	19.50	. . . .	. . . .	Positive	Positive	5 (or less)
4481	10.22 10.19	9.92 9.97 9.80	86.69	0.335	3.08	3.04	0.088	40.5	25.8–26	4.63	8.64 8.44	234.4	20.65	14.89 14.98	72–72.5	Positive	Positive	5
4482	12.81 12.86	13.01 13.06 13.18	82.18	0.56	4.13	4.07	0.18	39.6	25.5–26	4.88 5.00	10.50 10.18	238.8	21.66 21.94	11.86 12.27	72–72.5	Positive	Negative (slight tint)	. . . .
4490	12.31 12.40	12.82 12.83	82.96	2.18	2.03	2.00	0.408	39.8	26–26.5	4.67 4.88	8.58 8.37	236.8 235.3	20.7	11.92 12.23	72.5–73	Positive	Negative (slight tint)	
4501	13.47 13.46 13.50	13.57 13.51 13.59	83.29	1.54	1.61	1.61	0 255	42.0	42–43	4.21 4.29	7.10 7.13	228.0 228.8	26.45	20.4 19.89	72–72.5	Positive	Negative (very slight tint)	. . . .
4521	13.94 13.93 13.66	13.56 13.62 13.47	80.72	2.51	3.25	3.23	0.28	44 7	44–45	3.73	4.83	221.1 221.9	33.3 33.8	16.81	. . . .	Positive	Positive	20 (at least)
4624	10.00 10.19	9.36 9.54	86.84	0.75	2.96	2.93	0 063	39.7	25–25.5	5.44 5 59	10.95	237.83 237.79	24.91 24.67	9.99	73–73.5	Positive	Negative	
4632	15.81	15.87 15.77 15.83	80.57	1 24	2.37	2.34	0.80	41.2	43–43 5	4.82	9.02	228.3 227.4	18.24	8.28	. . . .	Positive	Positive	5–10
4850	10.89 10.95	11.00 11.11	84.06	2.11	2 77	2 77	0.26	41.1	.	4.19	9.40	228.3 227.1	17.56 17.90	11.99	. . . . . .	Positive	Negative	. . . .

*The Baudouin and Villavecchia tests for sesame oil were positive in the case of Sample No. 4311, only; the Settinj test for soy bean oil was negative in every case.

used for refining different oils in the same plant. It is not believed, however, that as much as 5 per cent could originate from this source.

As cottonseed oil is not derived from nuts, its presence in nut margarine in excess of a small amount that may be due to a contamination from refining machinery would appear to constitute adulteration.

SUMMARY.

1. Analyses, including the examination of the fat, are given of 15 samples, representing 15 different brands of nut margarine.

2. Special care is necessary in the preparation of the sample in order to obtain concordant moisture results.

3. The results show considerable variation in composition and proportion of the fats used, as revealed by wide ranges in certain physical and chemical characteristics.

4. The official methods for water, fat, curd, and salt were found applicable to this product.

5. Results on peanut oil by Evers' modification of Bellier's method indicate that this method can, with experience, be made to give results that are approximately quantitative when applied to nut margarine.

DETERMINATION OF FAT IN ALIMENTARY PASTE, FLOUR AND DRIED EGG.

By R. HERTWIG (U. S. Food and Drug Inspection Station, San Francisco, Calif.).

It is a recognized fact that the determination of fat in alimentary pastes and egg noodles by the direct extraction of the sample with dry ethyl ether[1] gives results considerably less than those for the combined fat of the ingredients entering into the product[2]. The same is true of bread[3]. Apparently the ether does not penetrate the hard glutenous particles sufficiently to extract all the fat. Unbroken plant cells may also prevent complete extraction. Disintegration of the sample with an acid and heat hydrolyzes the proteins and starch, disrupts the cell walls and liberates the fat so as to allow its easy extraction. In order to extract the fat from these products more completely, a method has been developed and designated an "acid digestion method". Groszfeld[4] applied the same principle of inversion for determining fat in bakery products.

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 72.
[2] *Z. Nahr. Genussm.*, 1913, 25: 717.
[3] Leach, Food Inspection and Analysis, 1920, 341.
[4] *Z. Nahr. Genussm.*, 1917, 34: 490.

Method for the determination of fat in alimentary paste, flour and dried egg.

Place 2 grams of ground sample in a 50 cc. beaker, add 2 cc. of 95 per cent alcohol, and stir so as to moisten all particles. Add 10 cc. of hydrochloric acid (sp. gr. 1.125) mix well, immerse the beaker in a water bath held at about 65°C., and stir at frequent intervals for 15–25 minutes, or until the proteins and starch are sufficiently hydrolyzed to form a clear solution. Add 10 cc. of 95 per cent alcohol and cool. Transfer the mixture to a Röhrig tube or a Mojonnier fat extraction tube; rinse out the beaker with 25 cc. of washed ethyl ether, in three portions, and shake well. Add 25 cc. of redistilled petroleum ether (b. p. below 60°C.) and mix well. From here proceed as directed under the official Roese-Gottlieb method for fat in milk[1]. re-extracting twice more with 15 cc. of each ether.

The moistening of the sample with alcohol prevents lumping on addition of the acid. The method, as described, is adapted to flour, alimentary pastes, and dried egg powder. It is believed that it is also applicable to bread and bakery products.

Results obtained by the acid digestion method and by the official direct method of fat extraction are shown in Table 1. The figures given are averages of duplicate determinations.

TABLE 1.

Results of determination of fat by direct extraction and acid digestion methods.

SAMPLE	MATERIAL	FAT	
		Direct Extraction	Acid Digestion
		per cent	*per cent*
A	Noodles, 7.7% egg solids	3.91	4.84
B	Noodles, 4.7% yolk solids	3.34	4.33
C	Noodles, 4.4% egg solids	2.10	3.77
D	Noodles, 4.5% yolk solids	2.81	4.24
E	Semolina	1.37	1.86
F	Flour	1.20	1.73
G	Semolina	1.22	1.93
H	Semolina	1.10	1.86
I	Dried Whole Egg	36.74	42.39

The fat extracted by the proposed method is perfectly clear when warm and dissolves in chloroform to a clear solution, leaving no residue. The fat extracted by this method from two egg noodles was found to contain much less lipin-phosphoric acid than the actual amount present, as determined by hot alcohol extraction or other methods[2]. The lipins of the wheat and egg are apparently more or less destroyed by the vigorous acid treatment. The method therefore determines those fats and fat-like substances which withstand the acid digestion.

The noodles used in these determinations (Table 1) were made up under the direct supervision of the writer or other representatives of

[1] *Assoc. Official Agr. Chemists, Methods*, 1920, 227.
[2] *Z. Nahr. Genussm.*, 1918, 35: 717.

the Bureau of Chemistry. From the formulas of three noodles (Samples B, C and D) and the analyses of the flour and eggs used in them, the theoretical fat content by the acid digestion method can be computed. Table 2 shows the calculated fat content and that actually recovered by the proposed method on the moisture-free basis.

TABLE 2.

Results showing fat content.

SAMPLE	MATERIAL	FAT		RECOVERY
		Calculated	Found	
		per cent	*per cent*	*per cent*
B	Yolk Noodle....	5.05	4.93	97.6
C	Whole Egg Noodle	4.31	4.26	98.8
D	Yolk Noodle....	5.12	4.79	93.6

The data in Table 2 indicate that the acid digestion method recovers practically all the fat from noodles that is contained in their component materials, as determined by the same method. This method, therefore, should be found very useful in calculating the egg content of noodles from their fat content after the average percentages of fat in flour and eggs, by the proposed method, have been established.

The lipin-phosphoric acid content of noodles, commonly used to compute the amount of egg present, is believed to diminish during storage[1]. Some constitutent which does not thus change would be more dependable for this purpose. The fatty substances determined by the acid digestion method very probably remain unaltered during storage. The egg content of noodles should therefore be calculated from the fat by this method to corroborate that calculated from the lipin-phosphoric acid.

[1] *Z. Nahr. Genussm.*, 1917, 34: 490.

INDEX TO VOLUME VI.

PROCEEDINGS OF THE SECOND AND THIRD DAYS OF THE THIRTY-SEVENTH ANNUAL CONVENTION, 1921, AND OF THE THIRD DAY AND PART OF THE FIRST DAY OF THE THIRTY-EIGHTH ANNUAL CONVENTION, 1922.